

DILUTE METAL RECOVERY FROM HYDROMETALLURGICAL
PROCESS WASTE STREAMS

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Dilute Metal Recovery from Hydrometallurgical Process Waste Streams

by

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A thesis submitted to the
School of Graduate Studies
in partial fulfillment of the
requirements for the degree of
Master of Engineering

Faculty of Engineering and Applied Science
Memorial University of Newfoundland
April 2008

St. John's

Newfoundland

Canada

Abstract

There have been a number of advancements in the area of waste treatment over the past decade, especially in mining industrial applications. Improvements have been made to conventional technologies to adapt to the tightening of waste disposal regulations. Trace metals in industrial effluents, once regarded as waste, now have the potential to be recovered as a valuable by-product.

Three separation technologies shown to be successful in mining industrial applications include: ion-exchangers, membrane separation processes, and bio-processing systems.

The primary objective of this research is to provide a single source of information for separation technologies that apply to the recovery or removal of metals from waste streams and by-product streams from industrial processes similar to Inco's hydrometallurgical process and to indicate where more research is required to determine the best separation technology. It also provides a framework for comparing technologies based on technical feasibility, compatibility with other operations, environment and safety concerns and cost.

Due to limited information available on the specifics of the INCO effluent stream, this thesis focuses on technologies available to metal processing facilities in general.

Key Words: Trace metal recovery, separation technologies, hydrometallurgy, wastewaterers

Acknowledgments

I would like to acknowledge the contributions of the following individuals to this thesis. I would first like to thank my supervisors Dr. Kelly Hawboldt and Dr. Yuri Muzychka members of the Faculty of Engineering and Applied Science in Memorial University of Newfoundland.

I would like to thank my parents Michael and Teresa Edge, and all my family and friends for their love and support.

I would also like to thank Ashley Willcott, a great source of strength and support. You hold a very special place in my heart for all that you have done. Thank-you for being someone I look up to and strive to be like on a daily basis.

Finally I would like to acknowledge the following for their monetary support: NSERC, ACOA, and INCO.

Contents

Abstract	i
Acknowledgments	ii
List of Tables	vi
List of Figures	vii
Nomenclature	x
1 Introduction	1
1.1 Problem Statement	2
1.2 Scope of the Research	4
1.3 Objective of Research	5
1.4 Thesis Outline	6
2 Background	7
2.1 Voisey's Bay Details	7
2.2 Hydrometallurgy	10
2.3 Process Description	12
2.4 Waste Regulations	22

2.5	Waste Stream Constituents / Properties	24
2.5.1	Toxic Metals	28
2.6	Separation Criteria	31
3	Ion-Exchange	32
3.1	Fundamentals	33
3.1.1	Equilibrium Conditions	33
3.1.2	Concentration Profiles and Breakthrough Curves	37
3.2	Ion-Exchange Process	39
3.2.1	Service	41
3.2.2	Backwash	41
3.2.3	Regeneration	41
3.2.4	Rinsing	43
3.3	Types of Ion-Exchange Units	44
3.3.1	Batch Operation	44
3.3.2	Column Operation	44
3.3.3	Moving Bed Operation	46
3.4	Resins	47
3.4.1	Inorganic Resins	48
3.4.2	Organic Resins	49
3.4.3	Selectivity of Ion-Exchange Resins	56
3.4.4	Effectiveness of Ion-Exchange	57
3.5	Applications in Industry	61
3.5.1	Feasibility Considerations	77
3.5.2	Process Limitations	78

3.6	Conclusions	80
4	Membranes	81
4.1	Fundamentals	82
4.1.1	Mass Transfer Laws	82
4.1.2	Mass Transfer Velocities	84
4.1.3	Diffusion Coefficients	85
4.2	Membrane Separation Process	88
4.2.1	Driving Forces	89
4.2.2	Membrane Characteristics	93
4.2.3	Membrane Material	94
4.2.4	Membrane Shapes and Modules	97
4.3	Membrane Types	100
4.3.1	Dialysis / Electrodialysis	111
4.3.2	Reverse-Osmosis	114
4.3.3	Ultrafiltration	121
4.3.4	Microfiltration	123
4.4	Conclusions	124
5	Biotechnology	125
5.1	Types of Microorganisms	127
5.2	Biomining	128
5.2.1	Biobleaching	129
5.2.2	Biooxidation	133
5.3	Bioremediation	133
5.4	Biosorption	134

5.5	Conclusions	140
6	Technology Comparison	142
6.1	Ion-Exchange	142
6.2	Membrane	144
6.3	Biotechnology	146
6.4	Qualitative Comparison	147
6.5	Conclusions	151
7	Conclusions	152
7.1	Recommendations	153
	References	154

List of Tables

2.1	Authorized Levels of Hazardous Substances [15]	23
2.2	VBNC Project Capacity at the Pilot Plant [11]	26
2.3	Preliminary Engineering Estimates of Waste Streams for VBNC Project [11]	26
3.1	Selectivity of ion-exchange resins in decreasing order [32]	57
3.2	Selectivity Coefficients of Sordolit Chelate Resin [47]	58
3.3	Composition of sulfide hydrometallurgy waste-water effluent [14]) . .	64
3.4	Commercial resin properties [14]	65
3.5	Distribution coefficients (K_D) of commercial resins (shown in Table 3.4) [14]	66
3.6	Characteristics of Lewatit TP-207 Resin [37]	75
4.1	Characteristics of membrane separation processes [52]	95
4.2	Characteristics of membrane separation processes (continued) [52] . .	96
5.1	Factors Influencing Mineral Oxidation and Mobilization by Microorganisms [80]	130
5.2	Metal Biosorption and Bioaccumulation Characteristics [3]	141
6.1	Performance Characteristics of Heavy Metal Removal / Recovery Technologies [3]	149

List of Figures

2.1	Location of the Voisey's Bay Deposits [8]	8
2.2	Voisey's Bay Site Map [8]	8
2.3	Mineralized Zones at Voisey's Bay [8]	9
2.4	Hydromet Pilot Plant Location: Argentia, Newfoundland [11]	13
2.5	Hydromet Commercial Scale Plant Location: Long Harbour, Newfoundland [10]	14
2.6	Conceptual Process Flow sheet for VBNC Hydromet Process [11] . .	16
2.7	Conceptual Process Flow sheet for the Hydromet Process [11]	20
2.8	Sample Hydromet Block Diagram	25
3.1	Adsorption Isotherm using Freundlich Trend [28]	34
3.2	Sample Breakthrough Curve for Ion Exchange Process [29]	36
3.3	Sample Ion-Exchange Operation a) Service period, b) Backwash period, c) Caustic regeneration, d) Acid regeneration, e) Resin miting [51]	40
3.4	Ion-Exchange Operation (a) co- and (b) counter-current-flow regeneration (H^+ form cation resin; Na^+ removal) [35]	42
3.5	Concentration Reduction of Y ion using a Column Type Ion-Exchange Unit [32]	46
3.6	Simplified Moving-Bed Ion-Exchange Unit [37]	47
3.7	Exchange Capacity vs. pH for Weak Acid and Base Resins[32]	50

3.8	Regeneration Capacities of Commercial Resins for Ion Exchange Process [32]	51
3.9	Molecular Formula of Ethylenediaminetetraacetic Acid (EDTA)[48] .	55
3.10	Conceptual Linear Plot of Moisture Content vs Crosslinkage [38] . . .	59
3.11	Moisture Content vs Cross linkage for Divinyl benzene adsorption[35]	60
3.12	Residual Concentration of Metals as a Function of pH [14]	66
3.13	Kinetics of the Simulation Loading of Metals in a Stirred Tank [14] .	67
3.14	Thermodynamic Dissolution Coefficients [39]	71
3.15	Equilibrium Isotherms for Sorption of Pb^{+2} ions for Duolite C26 Resin [39]	73
3.16	Elution Operation Mode for Column Type Ion Exchange [37]	76
3.17	Division Operation Mode for Column Type Ion Exchange [37]	77
4.1	General Membrane System [36]	89
4.2	Mass Transport Modes [53]	91
4.3	Facilitated Transport (Co-current and Countercurrent Transport) [53]	92
4.4	Materials and structures of membranes [53]	97
4.5	Membrane Shapes [36]	98
4.6	Membrane Modules [36]	99
4.7	Emulsion Liquid Membrane System [52]	102
4.8	Continuous Liquid Membrane Process [52]	103
4.9	Kinetic curves for the removal of zinc, lead, cadmium, and copper ions in ELMs [63]	107
4.10	Extraction of Cu^{2+} , Co^{2+} and Ni^{2+} with Alamine 336 vs. HCL concentration Using a SLM [61]	110
4.11	Bipolar Electro-Extraction Process for Separation of Co^{2+} and Ni^{2+} [59]	113
4.12	Use of integrated BM and Absorption unit for removal of Co^{2+} and Ni^{2+} ions [59]	114

4.13	Rejection model of mono- and bi-polar membrane in RO [60]	119
5.1	Examples of Typical Biosorption Processes - I [88]	136
5.2	Examples of Typical Biosorption Processes - II [88]	137
6.1	Qualitative Technology Comparison	150

Nomenclature

A	= mass transfer area
a_i	= activity
A_s	= solute permeability constant
A_w	= solvent permeability constant
A_x	= cross sectional flow area
BM	= bipolar membranes
B^{ZB}	= constituent cation (valuable species)
$B_{\nu B}Y_{\nu Y}$	= Solid ore being dissolved
C	= concentration of the residue (precipitate)
c	= amount of adsorbate/ m^3 of fluid [kg/m^3]
c'_b	= bulk solute concentration
c'_c	= solute concentration in the retentate
c'_w	= concentration of solute in feed solution at the membrane surface
c''	= concentration of the solute in the permeate solution
C_a	= concentration of the component of interest sorbed by the media
CCD	= counter-current decantation
$CCME$	= Canadian Council of Ministers of the Environment
C_f	= equilibrium concentration of the component of interest
C_i	= solution phase concentration
C''_i	= downstream bulk phase flow (permeate)
C'_i	= upstream bulk phase flow (feed or retentate)
c_L	= concentration of the liquid membrane
C_o	= concentration of the component of interest in the untreated solution (initial concentration)
COD	= chemical oxygen demand
c_s	= concentration of the solid membrane
$CSTR$	= continuous stirred tank reactor
c_{w2}	= solvent concentration on the product stream
c_1	= solute upstream concentration
c_2	= solute downstream concentration
Δc_i	= concentration difference across the membrane for species i
D_{AB}, DBA	= concentration gradient between components A and B
dc_i/dz	= concentration gradient in the z-direction
D_{eff}	= effective diffusion coefficient
$DPRV$	= volume of resin
D_s	= diffusion coefficient
DVB	= divinylbenzene

<i>EDTA</i>	=	ethylenediaminetetracetate
<i>ELM</i>	=	emulsion liquid membrane
<i>EMD</i>	=	equimolar counterdiffusion
<i>eq</i>	=	equivalent
<i>%E</i>	=	percent extraction
<i>f</i>	=	friction factor
<i>f_i</i>	=	fugacity
<i>f_w</i>	=	fraction of water recovery
<i>H_B</i>	=	calculated bed length to break point
<i>H_T</i>	=	total bed length
<i>H_{UNB}</i>	=	unused bed (experimental value)
<i>J_{iz}</i>	=	molar flux
<i>J_w</i>	=	water flux
<i>K</i>	=	experimental variable
<i>K'</i>	=	equilibrium distribution coefficient
<i>k'</i>	=	pseudo second order reaction rate constant of adsorption
<i>K_{A/B}</i>	=	relative molar selectivity coefficient or the equilibrium constant
<i>K_D</i>	=	distribution coefficient [<i>mcg/g</i>] - ratio of the concentration of the solute in the stationary phase to that in the mobile phase in equilibrium conditions
<i>K_s</i>	=	Solubility of the solute in the solvent
<i>K_{sp}</i>	=	solubility product
<i>k_t</i>	=	first order reaction rate constant of absorption
<i>K_w</i>	=	water mass transfer coefficient
<i>L</i>	=	phenomenological coefficient relating fluxes to driving forces
<i>l_M</i>	=	effective membrane thickness
<i>LM</i>	=	liquid membranes
<i>L_m</i>	=	membrane thickness
<i>m</i>	=	increase in the concentration of the common ion [moles/litre]
<i>M_B</i>	=	molecular weight
<i>[Me]_{org}</i>	=	concentration of metal of choice in organic solution
<i>[Mc]_{aq}</i>	=	concentration of acid (HCl)
<i>MEND</i>	=	mine environment neutral drainage
<i>MTZL</i>	=	mass transfer zone length
<i>N</i>	=	molar transmembrane flux
<i>n</i>	=	number of kgmol of solute
<i>n_c</i>	=	experimental constant
<i>N_i</i>	=	molar flux
<i>n_i</i>	=	molar flow rate
<i>N_s</i>	=	Solute flux
<i>N_w</i>	=	solvent flux

p	=	hydrostatic pressure
PAL	=	pressure acid leaching
p_i	=	partial pressure
P_M	=	permeability
\bar{P}_{M_i}	=	permeance
ppm	=	parts per million
P_w	=	membrane solvent permeability
ΔP	=	transmembrane pressure
ΔP_h	=	hydrostatic Pressure difference
Δp_i	=	permeability
Q	=	resin capacity
q	=	amount of adsorbate/adsorbent (solute/solid) [kg/kg]
Q_c	=	theoretical specific capacity
q_e	=	mass of metal absorbed at equilibrium
Q_f	=	quantity of feed
Q_i	=	volumetric flow
q_o	=	kg of adsorbate/kg of solid
Q_p	=	quantity of permeate
q_t	=	mass pf metal absorbed at time t
R	=	organic portion of the resin
R'	=	intrinsic membrane solute rejection
r	=	water recovery
R_A	=	radius of the solute molecule
R_c	=	cake resistance
R_g	=	universal gas constant
R_m	=	membrane resistance
RO	=	reverse osmosis
R_r	=	observed solute rejection
S	=	solubility
SLM	=	supported liquid membrane
T	=	temperature
TFC	=	thin-film composite (membranes)
t_b	=	time to breakthrough
$TCLP$	=	toxicity characteristic leaching procedure
t_t	=	time equivalent to the total capacity
Δt	=	time step

UF	= ultrafiltration
$ULPROM$	= ultra-low pressure reverse osmosis (membrane)
UMD	= unimolecular diffusion
V	= volume of effluent solution
v	= linear velocity
v_A, v_B	= component velocities
v_a	= concentration of the component of interest
$VBNC$	= Voisey's Bay Nickel Company
v_i	= mixture velocity
v_{iD}	= diffusion velocity
v_m	= molar average velocity of the mixture
V_m	= volume of pure solvent
V_o	= batch volume
X	= generalized driving force
X	= mass of the separation media
x_i	= concentration fraction
Y^{ZY}	= anion (contaminant species)
y_i	= mole fraction species i
z_i	= ionic valence of the species
$[ion]$	= an ion/ionic group enclosed in square brackets denotes concentration

Greek Symbols

α_{ij}	= separation factor for two species i and j
ϵ	= volumetric fraction of interstitial water
ϵ_K	= fractional porosity
ϕ	= osmotic coefficient (ratio between actual and ideal osmotic pressure)
ϕ_B	= association factor of the solvent
ϕ_e	= electrical potential
$\delta\phi$	= osmotic pressure difference between feed and production solutions
γ_i	= activity coefficient
μ	= viscosity of the solvent
μ_B	= solvent viscosity
μ_i	= chemical potential
$\nabla\mu_s$	= solute chemical potential gradient
$\nabla\mu_w$	= water chemical potential gradient
π	= osmotic pressure for dilute water solutions
$\Delta\pi$	= transmembrane osmotic pressure gradient
σ	= surface tension
τ	= pore path tortuosity
\mathcal{P}	= parachor defined as $\nu\sigma^{1/4}$

Chapter 1

Introduction

The mining industry is constantly improving through technological innovations, enhanced knowledge of environmental issues, and increasing demand for metal products. Dilute waste streams once considered to be uneconomical for enhanced metal refinement are now being treated for additional recovery for economic purposes, environmental reasons, or both. Improvements in processing technologies have resulted in decreased operation time, higher energy efficiency, minimal use of added chemicals, lower operational pH and temperature values, and improved waste management systems which benefit mining companies as well as the surrounding environment.

The increase in knowledge in areas of hazardous wastes, environmental impacts, and waste management technologies, has shifted the focus from on-site management to remediation and pollution prevention. The field of waste management is multidisciplinary and involves the management of wastewater, process effluent, groundwater, and solid wastes that affect the environment and human health.

Research is being conducted on a variety of levels to accomplish a common goal; to reduce the amount of waste in the effluent streams exiting the mineral processing

industry and to recover maximum amounts of product from these effluent streams using specific separation techniques.

1.1 Problem Statement

There are a number of challenges in extractive metallurgy of non-ferrous metals and advanced materials. The area of greatest challenge involves the field of treatment of metallurgical wastewaters and residues for product and by-product recovery and detoxification [1].

In order for a process to become more economical there needs to be a reduction in the contaminant in the effluent. This is accomplished by the recovery of as much of the valuable metals, and other contaminant metals, as possible. There are a number of issues to consider with the treatment of wastewater from the hydrometallurgical process. First, the low values of by-product metals in the effluent streams require equipment that can effectively remove metals present in dilute concentrations and secondly, the need for processing technologies that can handle the high flow rates that typically leave these industries [2].

Due to the volume and toxicity, all major waste streams from the hydrometallurgical process are considered to impact the surrounding environment. The physical and chemical environmental impact of these waste streams is a function of the waste that is generated at each stage of the process (i.e. quantity and content of heavy-metals). It is therefore necessary to have a detailed understanding of the waste stream constituents exiting the major sections of the processing plant to ensure that the most effective and efficient waste reduction technologies are implemented.

Inco has acquired the rights to develop the Voisey's Bay nickel-copper-cobalt deposits discovered in northern Labrador. Upon completion of a number of feasibility studies, it was determined that the novel use of a hydrometallurgical process facility that utilizes an atmospheric and pressure leaching system will be researched and possibly developed. Due to the specific composition of the ore and the use of a novel and innovative process, the waste generated in Voisey's Bay hydrometallurgical facility is proprietary. However, bulk properties of typical waste streams from hydromet facilities have been determined from literature. At present, the characteristics of the effluent stream from INCO's hydrometallurgical process are unavailable. Specific analysis and selection of processing technologies based on INCO's effluent stream is not possible. The objective of this research is to investigate possible technologies that will reduce or recover the amount of contaminants present in a waste stream from a metal processing facility and provide a framework for technology selection for future research.

Metals are a class of pollutants, often toxic or dangerous, widely present in industrial wastewater [3]. The term heavy-metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. From a toxicity perspective, the contaminants that are of most concern in wastewater include: mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb) [4].

This research presents a study of the available separation technologies that will support the reduction and treatment of dilute metal waste stream constituents. Three major separation technologies that are applied in industrial waste treatment applications include ion-exchange, membrane separation, and bio-processing of materials. The type of metals present in the waste stream, the amount of separation required,

and the flow rates involved all play a role in choosing the appropriate separation technology.

Further extraction of metals from the by-product streams can potentially increase the revenue generated throughout the project's life time. Each treatment alternative has distinct advantages and disadvantages which need to be analyzed in greater detail once specific details of the waste stream is known. Typical distinguishing parameters for comparing the technologies include cost, feasibility, compatibility and environmental impact. Technical, environmental, and economical issues need to be addressed when considering each of the treatment alternatives.

1.2 Scope of the Research

In the initial stages of the research, an in depth analysis of the hydrometallurgical process was conducted for pyrite / pyrrhotite production. This involved understanding the individual steps that take place including i) leaching (mid-low temperature), ii) solid & liquid separation, iii) electrowinning, and iv) neutralization. Research was conducted in the attempt to uncover examples of hydrometallurgical processes that have been used to process nickel-copper-cobalt sulphide products comparable to the Voisey's Bay project. It was hopeful that a comparable process would be discovered that would offer a break down of typical waste stream constituents exiting the various stages of the hydrometallurgical facility. Due to the fact that the hydromet process to be implemented for the Voisey's Bay project is a novel technology, information was collected from processes that were similar but not identical.

Regulations and restrictions imposed by the Provincial and Federal Governments were analyzed. This allowed for a general understanding of the restrictions that are

imposed by the various governing bodies, providing a better picture of reduction goals for the technologies considered.

Technologies that can be used to treat dilute metal concentrations were examined. Currently there are a wide variety of technologies at the research stage that have not yet been applied at an industrial scale. Less emphasis was placed on these technologies since they were determined to have a high associated risk factor. Particular focus was given to the ion-exchange process, membrane technologies, and bio-processing techniques.

It should be noted that research and development in the operation of the hydromet demonstration plant are ongoing and additional information obtained from experiments conducted at the mini-pilot plant and the pilot plant will lead to process improvements. Updates are constantly being made to Inco's hydromet process to ensure that maximum extraction is achieved with minimum harm to the surrounding environment.

1.3 Objective of Research

The main objectives of the research are:

- To study the INCO specific hydrometallurgical process.
- To identify waste stream constituents in a hydrometallurgical application or similar process.
- To evaluate the regulatory disposal guidelines and standards for mining waste products (provincial and national levels).

- To identify the possible separation technologies available to treat the previously identified waste streams.
- To provide framework for comparing technologies for future research.

1.4 Thesis Outline

This thesis consists of seven chapters. Chapter 1 is the introductory chapter that presents the problem statement, scope of research, and the objectives of the research. In Chapter 2 a descriptive background is given with respect to Inco's Voisey's Bay project, the hydrometallurgical process, process description, waste regulations, possible waste stream constituents according to the literature review conducted, and a list of separation processes examined for dilute metal recovery. Chapter 3 provides detailed information on the ion-exchange process including its applicability toward dilute metal concentrations. Membrane separation technologies are explored in Chapter 4. Chapter 5 demonstrates the possible use of bio-processing for waste reduction. Chapter 6 provides a qualitative breakdown of technologies explored and the thesis is then concluded in Chapter 7.

Chapter 2

Background

2.1 Voisey's Bay Details

The Voisey's Bay nickel-copper-cobalt deposits were discovered in September 1993 by prospectors Al Chislett and Chris Verbiski on the Eastern edge of a vast expanse of northern wilderness 35 km southwest of Nain, Labrador: Figure 2.1. The deposits are contained within igneous rocks that were formed approximately 1.3 billion years ago [6]. In 1996 Voisey's Bay Nickel Company (VBNC), a wholly owned subsidiary of Inco Ltd., acquired rights to the Voisey's Bay property and in June 2002, Inco announced that an agreement had been reached with the Government of Newfoundland and Labrador on a plan to develop the Voisey's Bay deposits [7]. Figure 2.2 shows the proposed Voisey's Bay site map where the mining and concentrating of the ore will take place.

The location of the mineralized zones at the Voisey's Bay site is shown in Figure 2.3. One zone, known as the "Ovoid", has surface dimensions of approximately 800 meters by 350 meters, extending 125 meters in depth and will be mined using open pit methods. As of the end of 2002, the Ovoid deposit contained an estimated



Figure 2.1: Location of the Voisey's Bay Deposits [8]



Figure 2.2: Voisey's Bay Site Map [8]



Figure 2.3: Mineralized Zones at Voisey's Bay [8]

proven and probable mineral reserve of 30 million tonnes grading 2.85% nickel, 1.68% copper, and 0.14% cobalt. In addition, there is an estimated 54 million tonnes of indicated mineral resources grading 1.53% nickel, 0.70% copper, and 0.09% cobalt; and 16 million tonnes of inferred mineral resource grading 1.6% nickel, 0.8% copper and 0.1% cobalt available as part of the Voisey's Bay project [8]. Further exploration work will be conducted to determine the amount of minerals that can be mined and the appropriate mining techniques applicable for extraction [6].

The minerals are found within three deposits: the "Eastern Deeps" zone located 1 km east of the Ovoid, the "Discovery Hill" located 1 km west of the Ovoid, and the "Reid Brook" deposit located 2 km west of the Ovoid. The Ovoid is close to the surface (beneath 2.5-30 meters of overburden) while the depths of the other deposits vary be-

tween 100 and 1000 meters below the surface [6]. All mineral zones consist of nickel sulphide (pentlandite, $(FeNi)_9S_8$), which contains the cobalt, copper-iron sulphide (chalcopyrite, $CuFeS_2$) and iron sulphide (pyrrhotite, $Fe_{(1-x)}S$). The style of mineralization varies from massive (over 90 percent sulphide minerals) to disseminated (the sulphides are mixed with other minerals) [6].

2.2 Hydrometallurgy

Hydrometallurgy, also known as hydromet, is a mineral processing technology that combines water, oxygen and other chemicals in a pressurized vessel to dissolve valuable metals from its ore, concentrate or intermediate product such as a matte (ore that is partially processed through a smelter). The goal of the hydromet process is to obtain metal product solution (containing both impurity metals and valuable metals) that must be purified chemically in order to recover the valuable metal in the form of a pure product and waste components (such as rock, iron oxides, and sulphur) in a solid residue that can be disposed of in an environmentally responsible manner [9].

Hydrometallurgy is not a new technology, it has been used for many years for the processing of zinc, copper, and nickel mattes [9]. Over 200 processes world-wide use some form of the hydromet process for extracting metals directly from ores or from concentrate [6]. A major improvement in the technology came about in the mid-1990s when an acid-oxidative hydromet process was developed for processing nickel sulphide concentrates [8]. This development evolved into a pressure acid leaching (PAL) technology that directly processes nickel sulphide concentrate to produce a high purity electronic nickel without having to first smelt the concentrate. "Inco's innovative proposal for Voisey's Bay processing applies state of the art technology to nickel

sulphide concentrate” [9].

Traditionally the production of metals occurred in two steps: smelting and refining in a process called pyrometallurgy. Pyrometallurgy is a processing method that is used for mined ores and involves the use of high temperature reactions to process minerals. In recent years, the nickel industry has smelted concentrates produced from nickel, copper, and cobalt sulphide ores to make an intermediate product (matte) and then refined this product using the hydromet process to produce high purity metals [10].

The distinguishing factor of hydrometallurgy is that some of the chemical reactions that occur during the sequence of events take place in an aqueous solution. The hydromet process is a more economical and environmentally friendly process, compared to pyrometallurgy, since the sulphur dioxide and dust emissions from the smelting process are eliminated and the wastes that are generated in the system can be easily contained and removed in a safe manner. In the hydromet process, the sulphides are transformed into elementary sulphur, which together with iron oxide, form solid tailings that can be neutralized to form a stable residue. The tailings will also contain gypsum and unleached rock mineral at a neutral pH [9]. Through the use of hydrometallurgy it is estimated that there will be an increase in the recovery of valuable metals normally lost during the smelting process, a decrease in energy consumption, as well as economic and environmental long-term benefits.

In order to ensure effective results using the newly developed processing technologies it is necessary to: confirm the processes technical and economical viability; allow for proper selection of materials for construction; and to examine the best way to handle and dispose of the wastes from the hydromet process. Inco has outlined a step-by-step research and development approach that is to be followed: [8].

- i) Prove that each step of the chemical process works individually at a laboratory scale.
- ii) Operate a mini pilot plant at laboratory facilities to ensure steps can be interconnected in a continuous process.
- iii) Build a demonstration plant in order to allow for fine tuning and optimization of the process.
- iv) Design and build the commercial hydromet facility capable of full scale operation.

Research and development will lead to better predictions of chemical reactions, evaluation of chemical and mechanical engineering of the process, specification of mechanical equipment and design, and method of operation of the plant[10].

2.3 Process Description

The demonstration pilot plant will be built in Argentia, Newfoundland on the Avalon Peninsula, Figure 2.4 while the commercial scale plant will be located in Long Harbour, Newfoundland. All the nickel concentrate originating from the Voisey's Bay mining operation will be processed at this processing plant.

Voisey's Bay mill/concentrator in Labrador will produce a finely ground nickel-rich concentrate (approximately 25% nickel) with a 10% moisture content to be exported from the mine via ship to the processing facility. The primary output will be a commercial grade nickel product (electronic nickel), but it will also produce cobalt and copper, both of which are contained in the Voisey's Bay nickel concentrate. The projected recovery rates are 95% for both nickel and cobalt, and 65% for copper

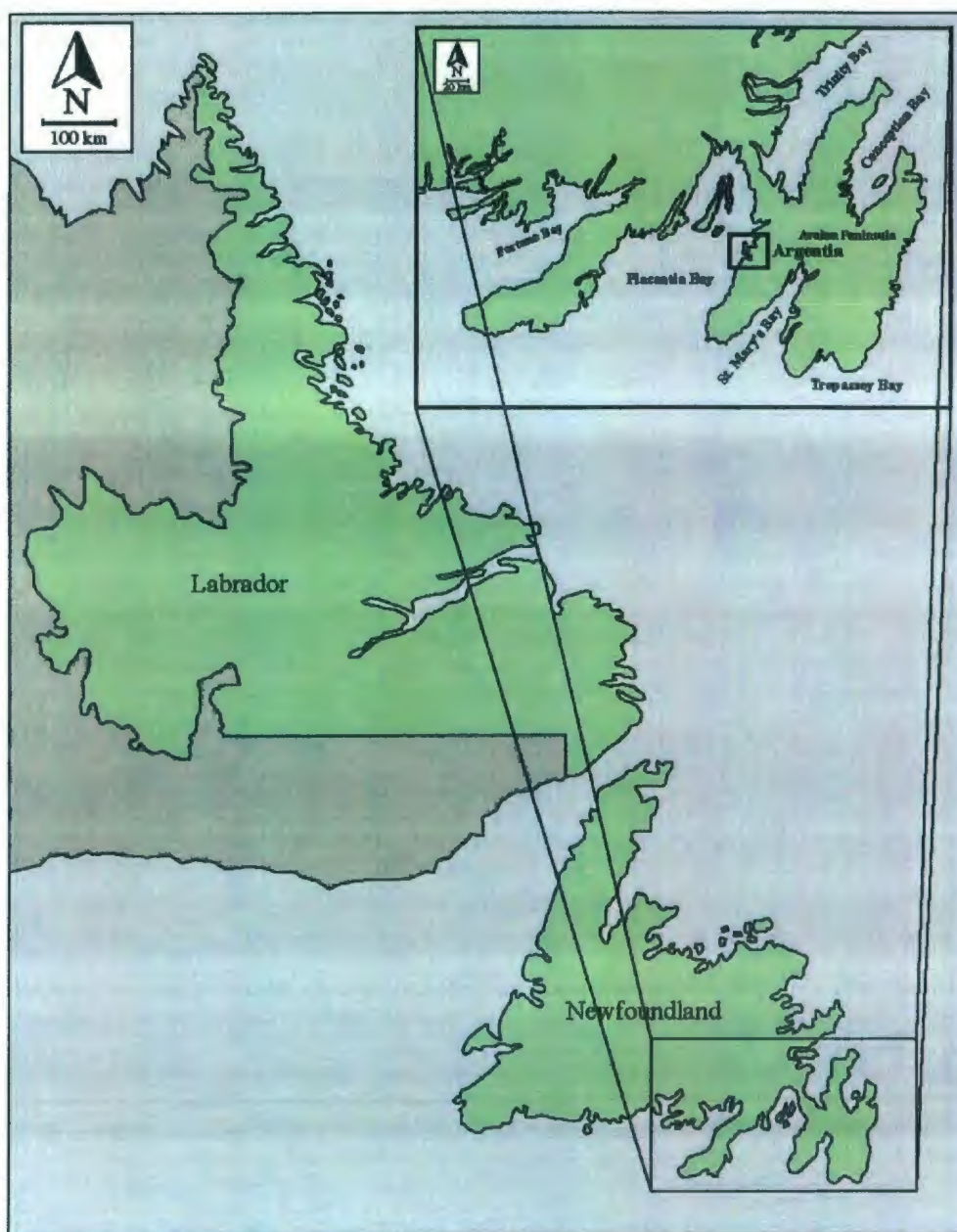


Figure 2.4: Hydromet Pilot Plant Location: Argentina, Newfoundland [11]

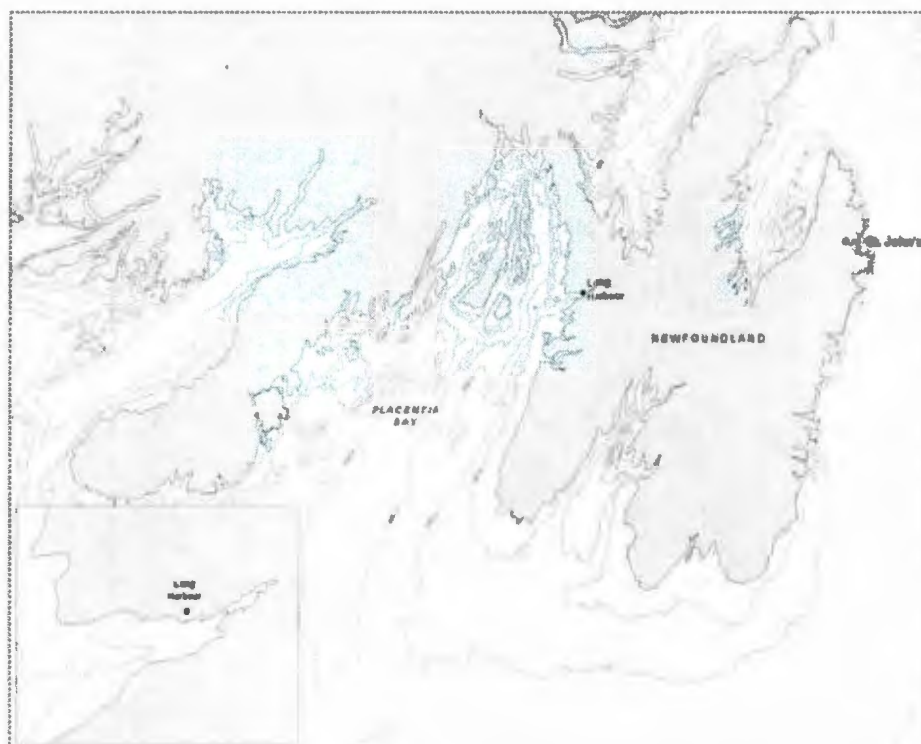


Figure 2.5: Hydromet Commercial Scale Plant Location: Long Harbour, Newfoundland [10]

[8, 11].

The goal for the Voisey's Bay Project is to construct a plant that will treat the nickel/cobalt/copper concentrate or a matte using either a hydromet or matte facility. In the case of a hydromet facility the feed stream will consist of a nickel concentrate that will be processed for the recovery of nickel copper and cobalt. The matte facility, on the other hand, will process a smelter produced nickel-bearing matte which will then be processed to recover the metal constituents. Another difference between the two processing facilities is that the hydromet plant uses a chloride-sulphate medium while the matte plant uses a sulphate medium only[10]. Differences can also be seen in the quantities and types of residues that are produced in these processes. The hydromet process will require large amounts of leach residue which requires subsea

storage in order to avoid the oxidation of elemental sulfur producing sulfuric acid. There will also be gypsum and iron hydroxide wastes involved. The matte plant will have mostly gypsum waste which can be stored above ground. Efforts are being made on all fronts to choose a technology that will provide the best technical and economical results. The focus of this thesis is on the opportunities involved in the use of a hydromet facility.

There are three main operations used in the hydrometallurgical process [12]:

- (i) Leaching of the ore or of an intermediate metallurgical product with acid, caustic, or a complex forming solvent, often combined with oxidation.
- (ii) Purification of the solution by precipitation of insoluble compounds or cementation of unwanted metals.
- (iii) Precipitation of wanted product, either as an insoluble compound or as a metal, either by chemical or electrochemical methods.

Figure, 2.6, shows a conceptual process flow sheet for the treatment of nickel concentrate specific to the Voisey's Bay project.

The following sections describe in more detail the steps that take place in the processing of nickel-copper-cobalt sulphide using the hydromet process: [10, 11]

Crushing and Grinding

The ore concentrate will be received at the processing site from shipments origination from the Voisey's Bay concentrator plant. The product will be stored in a concentrate storage building until needed for processing. In order to break up fused or lumpy materials and to provide a suitable particle size for further treatment, the concentrate

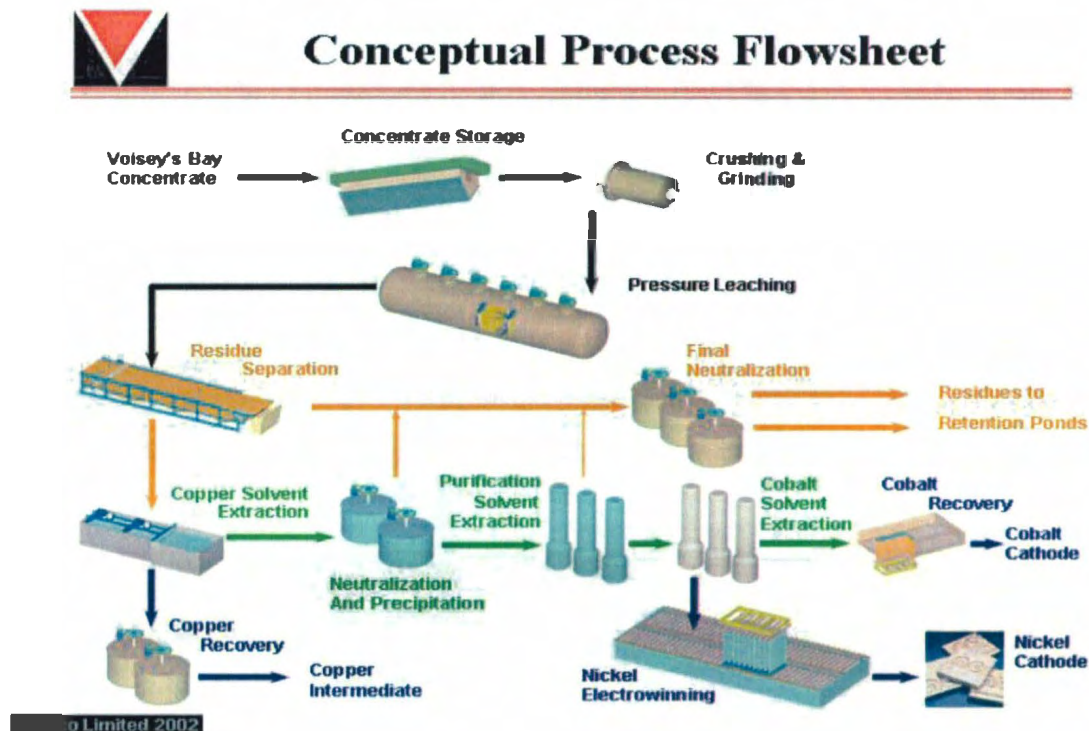


Figure 2.6: Conceptual Process Flow sheet for VBNC Hydromet Process [11]

is crushed and ground into a fine powder using a roll crusher, ball mill, and fine grinding mill. Approximately 80% of the concentrate will pass 20 micron. It is then mixed with recycled process water to produce a paste-like slurry which is stored in tanks for the subsequent leaching stage.

Leaching

Leaching is defined as the treatment of ores, concentrates and other metal-bearing materials by an acidic wet process that dissolves soluble minerals and recovers them into a pregnant leach solution [13]. Leaching processes in hydrometallurgy form a solution containing the metals that are to be recovered in the system. There are two types of leaching present in the proposed hydromet plant, atmospheric pre-leach and the pressure oxidative leach.

- *Atmospheric pre-Leach*

The feed is leached in a continuous stirred tank reactor (CSTR) with oxygen and chlorine gases. The O_2 and Cl_2 gases come from the nickel electrowinning circuit and are compressed to be utilized for leaching. This leach stage takes place at atmospheric pressure and is sometimes referred to as the chlorine pre-leach. The concentrate is then pumped into a large pressure cooker called an autoclave for the next stage, the pressure oxidative leaching.

- *Pressure Oxidative Leach*

The pre-leach concentrate is fed to the second leaching stage. This takes place in an autoclave at elevated temperature of $150^\circ C$ and pressure of 150 psig. Oxygen is injected into the autoclave and will react with the nickel, cobalt, and copper sulphide minerals to form liquid or solid sulphur and sulphuric acid. Once the sulphides are broken down by this process, the associated metals to which they were once bound are free to dissolve into the acidic solution.

The product of the autoclave system is a complex mixture of liquid or solid sulphur, an acidic solution of desirable and undesirable metals, and insoluble waste rock. The discharged slurry is cooled in a single stage of pressure let-down, known as flashing, to atmospheric pressure in a flash vessel. This results in the generation of some steam and the concentration of the metal solution.

This process takes place in corrosive conditions sufficient to dissolve most metals therefore anti-corrosive coatings, for example, titanium and linings such as acid-resistant brick, are required for the process equipment. Once the solution is flashed,

the process takes place at atmospheric pressure in fiberglass and plastic, tanks, and piping.

Filtration & Clarification & Neutralization

Once the hot leach slurry has been discharged through a pressure let-down vessel and the slurry is cooled allowing the molten sulphur to solidify - the next stage of filtration, clarification, and neutralization takes place. Using a process called counter-current decantation (CCD), the waste rock and sulphur are washed in stages with spent process solution and process water. This ensures that the maximum amount of dissolved metals are removed from the waste material. The leach residue, containing stable iron and sulphur compounds, will then be thickened, filtered, and sent to a final neutralization stage where limestone and lime are added for pH adjustment prior to impounding. Limestone is used to raise the pH and precipitate metals. It has the lowest material cost and is the safest and easiest to handle. The residue from the process is then pumped to a secure containment area.

The resulting solution contains all three desirable metals: nickel, cobalt, and copper, but will also include some undesirable metals such as iron. Air and limestone is added to the solution to oxidize iron, neutralize the pregnant leach solution and to help precipitate out a mixed iron and gypsum product. All water leaving the plant will be processed to remove contaminants.

The feed will then go through a number of chemical purification steps, enter settling tanks where it will undergo solid / liquid separation, removal of impurities and separation of Ni, Co, and Cu.

Solvent Extraction and Electrowinning

The iron-free solution is fed into a three stage solvent extraction set-up. In the first stage of the metal recovery section, the leach solution will be sent through a copper solvent extraction circuit. The unspecified copper extractant is dissolved in an oil diluent and contacted in stages with the metal solution. The copper dissolves in the extractant oil, leaving behind nickel, cobalt, and other minor metals. The oil extractant will be brought into contact with an acidic water solution where it will be stripped, resulting in a strong copper solution in acidic water. It is then sent to be electroplated in a process known as electrowinning.

Electrowinning takes place in a tank in which two conducting plates are inserted and an electric current is applied. The electricity flows from one plate through the solution to the other. The desired metal deposits on one plate to form a solid sheet. Using this process, a strong copper solution in acidic water will form into thick, commercially viable copper sheets.

The acidic copper-free leach solution together with a portion of the spent nickel electrolyte solution will react with limestone and lime to neutralize the solution and to precipitate gypsum. The gypsum solids will be filtered and sent to final neutralization and disposal.

The neutralized copper-free solution will be sent to the purification solvent extraction circuit to remove calcium, zinc, and other remaining trace impurities. This circuit uses an unspecified organic extractant to selectively remove the impurities, leaving a purified nickel-cobalt sulphate solution. The impurities will be stripped using an acid solution and sent for final neutralization and disposal.

The purified nickel/cobalt solution will be sent for cobalt solvent extraction where another organic solvent selectively extracts cobalt. The cobalt will be stripped from

the unspecified organic solvent by an acidic solution, producing a concentrated cobalt solution, which is then sent to a cobalt recovery circuit. The cobalt will be recovered in a cobalt electrowinning circuit.

The cobalt-free nickel solution will be sent to nickel electrowinning circuit where nickel metal will be deposited onto charged electrodes. The remaining product is pure nickel product in the form of thick sheets. The majority of the spent nickel electrolyte solution will be recycled back to the pre-leach and pressure leach. Oxygen and chlorine gas, produced as part of the nickel electrowinning reaction, will be collected and returned to the pre-leach.

The steps of the hydromet process is shown in the following block diagram[10]:

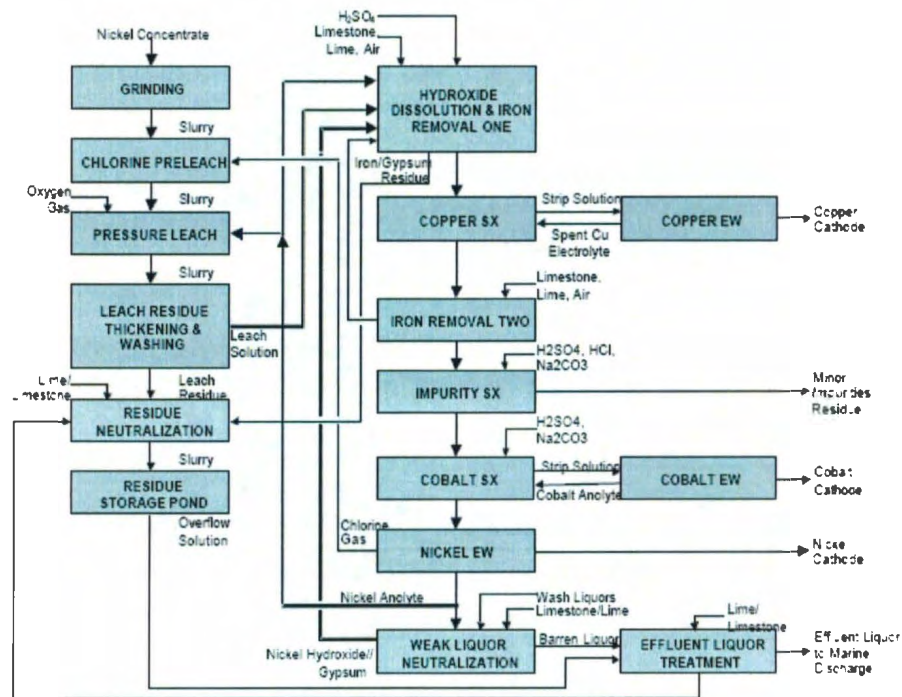


Figure 2.7: Conceptual Process Flow sheet for the Hydromet Process [11]

Stated in Voisey's Bay project registration[10] there are a number of inputs and

outputs expected from the facility. The major inputs are:

- Nickel concentrate
- Oxygen
- Limestone
- Lime
- Air
- Sodium chloride
- Hydrochloric acid
- Sulphuric acid
- Sodium carbonate
- Electric powers
- Water
- Extractants used to remove impurities or extract valuable species

The major outputs expected include:

- Nickel, copper, and cobalt
- Treated solid residue containing primarily iron oxides and hydroxide, elemental sulphur and gypsum with trace amounts of un-reacted nickel concentrate.
- Treated liquid effluent

2.4 Waste Regulations

The control of toxic metal wastes has become an important issue in recent years due to the increasing environmental regulations concerning their disposal. Waste management responsibilities include disposal, treatment, reduction, recycling, segregation, and modification.

The regulations that are imposed for waste management in the mineral industry vary depending on the the province in which the mining takes place and is a function of the type of metal that is being processed. There are a number of wastes generated by the mining industry, all of which have a varying degree of impact on the surrounding environment. Three major wastes considerations in the mining industry are acid mine drainage, mine tailings, and wastewater effluent. Acid mine drainage is low pH drainage water from certain mines usually caused by the oxidation of sulphides to sulphuric acid. Mine drainage can also contain high concentration of metal ions which are harmful to the environment. Mine tailings are the material that remains after valuable metals have been removed from the ore during milling. Wastewater effluents are raw (untreated), partially or completely treated liquids that flow from a facility.

The mine environment neutral drainage (MEND) [16] program is a joint effort between Canadian mining companies and provincial/territorial and federal departments to reduce the liability due to acid mine drainage. Acid mine drainage is the largest environmental liability facing the mining industry and the public through abandoned mines. Since the development of this program there has been a large amount of progress with regards to mines that are no longer in use. The current focus is to ensure the development of new mines that will operate without the risk of long term

effects upon closure.

The Environment Protection Act and Waste Management Regulations [17] deal with landfills and waste that contains metals. Wastes must be verified to be non-hazardous through a Toxicity Characteristic Leaching Procedure (TCLP) where the waste is soaked in acidic solution and the amount of contaminants that leach out is measured. If this exceeds the CCME (Canadian Council of Ministers of the Environment) guidelines the waste will be characterized as hazardous and would require disposal at a hazardous waste disposal site.

The Mining Act requires a submission of a Development Plan (updated annually) which outlines the mode of development of the project (including any additional processing steps), and must demonstrate prudent resource management.

The maximum concentration of metals that can be discharged into the environment is regulated by Environment Canada, Minerals and Metals Division. The Water Pollution Prevention and Control in the Canadian Mining Industry outlines the following disposal limits shown in Table 2.1 [10, 15]. Limits are based on best practical technology determined by a joint federal-provincial-industrial task force.

Table 2.1: Authorized Levels of Hazardous Substances [15]

Substance	Max.Authorized Monthly (mg/l)
Arsenic	0.5
Copper	0.3
Lead	0.2
Nickel	0.5
Zinc	0.5
TSS	30

2.5 Waste Stream Constituents / Properties

Specific waste stream constituents and properties could not be fully characterized for INCO's hydromet facility. Based on the research conducted, the closest example waste stream is shown in Table 3.3 for a sulfide hydrometallurgical facility. Even with this sample information available, the type and concentration of metals along with the chemical reactions may not be comparable to the nickel/cobalt/copper extraction process at INCO. Selecting a separation technology on a waste stream that may not be comparable to the waste stream of interest offers little value at this stage. Refer to the Recommendations section of this thesis for areas for future growth and advancement.

Figure 2.8 shows the block diagram of the hydromet process. Based on the figure, the two effluent streams that are to be considered for possible metal recovery, toxicity reductions, or both are:

- stream from impurity removal
- final neutralization solution

All steps in the hydromet process serve two major purposes: to put the metals of interest in a liquid form and to separate the desired metals from the unwanted materials in the form of precipitates. Once each metal is isolated in a liquid solution, electro-chemistry is used to recover the metals as solids [9].

Issues to consider in the treatment of dilute metals include limitations imposed by low concentrations in the waste stream. The pH of inorganic waste streams, unlike their organic counterparts, have variable pH that can be difficult to model when considering various separation technologies. Finally, the presence of other inorganic

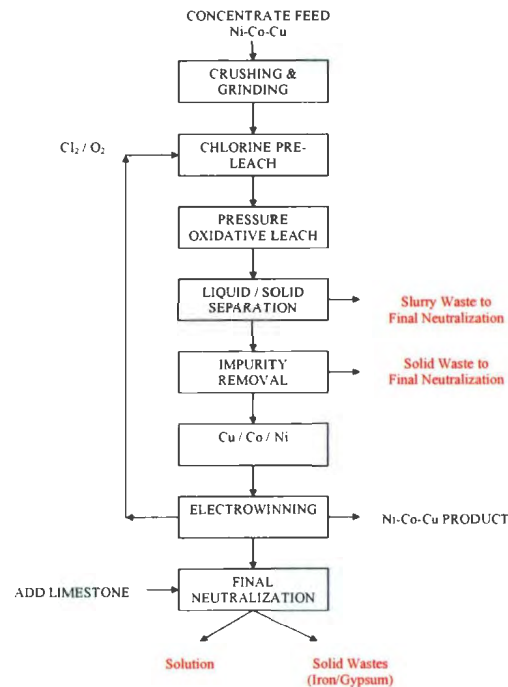


Figure 2.8: Sample Hydromet Block Diagram

materials in the waste streams can also have a negative impact on the separation efficiency, since they often compete with the metal of interest in the removal process.

Outputs expected from the facility are shown in Table 2.2:

Solid waste (non-hazardous) will be trucked by certified waste haulers to approved landfill sites. VBNC will have a waste reduction and recycling program during all phases of the project in order to minimize waste. The quantities of wastes produced at the facility has not been finalized since the project is still in development phases.

Table 2.2: VBNC Project Capacity at the Pilot Plant [11]

Component	Annual Capacity (tonnes)
Concentrate Feed	2000
Nickel in Feed	400
Copper in Feed	28
Cobalt in Feed	19
Leach Residue	1800
Gypsum Residue	1700

The preliminary engineering estimates of waste streams and quantities generated at the pilot plant are shown in Table 2.3.

Table 2.3: Preliminary Engineering Estimates of Waste Streams for VBNC Project [11]

Item	Preliminary Estimated Quantity
Leach Residue	1800 tonnes/year
Gypsum	1700 tonnes/year
Process Liquid Effluent	20,000 m^3 /year
Total Liquid Effluent (including site run-off)	108,000 m^3 /year
Autoclave Vent Gas (steam + O_2)	700 m^3 /year
Chlorine Scrubber Vent Gas (air with trace Cl_2)	1000 m^3 /year
Hydrogen Sulphide Scrubber Vent Gas (air with trace H_2S)	1000 m^3 /year
Process Tanks Vent Gas (air and water vapor)	1000 m^3 /year

The current plan is to have three residue storage ponds, approximately 7000 m^3 each, and associated piping to accommodate three years of residue storage. The residues that will be stored in this fashion include leach residue (iron oxide and sulphur) and gypsum. The ponds will be constructed with a liner system with a leakage detection and collection system to ensure maximum protection of the environment.

Also, effluent or polishing ponds of approximately 12,000m³ and associated piping and pumps will be constructed to receive run off and effluent overflow from the residue ponds.

The various waste streams from the demonstration plant will be directed to the final neutralization circuit. At this stage, the residue slurry will be treated in stirred reactors by pH adjustment and oxidation to neutralize the solutions, precipitate the trace metals, and stabilize the solids prior to discharge to the tailings pond.

Life cycle studies have been performed and have indicated that the environmental impact of hydrometallurgy is approximately one half of the impact of the traditional pyrometallurgy process in almost all categories studied. In using the hydromet process, there is a reduction in the amount of released airborne particles and gaseous emissions and a reduction in energy consumption compared to conventional smelting and refining. Although the methodology used to come to this conclusion is not clear, the results of the study have been made public on INCO's website.

VBNC considered both hydro- and pyro-metallurgical technologies, hydrometallurgy was chosen for testing at the facility since it had lower capital costs and potential for environmental benefits. Another alternative that was considered was the use of a bioleaching processing. This option was eliminated due to the high quantities of residues and neutralizing agents required and the costs of the process were considered high.

The components of the waste stream in the hydromet process is a function of the process specifics and therefore without knowledge of the operational specific breakdown in the Inco hydromet stream it is difficult to determine feasible separation technologies. However, in the following sections of the report some of the common separation

technologies that are currently used in industry are outlined based on a literature review on the removal of metals from dilute solutions and solid separation.

2.5.1 Toxic Metals

In the hydromet process, metals and other chemical additives exist in the effluent streams at concentrations that can be hazardous to the surrounding environment if left untreated.

Metals that have the greatest concern for the environment are those which have a toxic or inhibitory effect on living things. It is important to note that other environmental conditions such as pH, temperature, and water hardness will also affect the toxicity. Metals that are of concern include cadmium, chromium, copper, cobalt, lead, nickel, and zinc.

Due to limited information available specific to the hydromet process it was found that in the electroplating industry the metals that are typically of concern include cadmium, zinc, copper, chromium, mercury, lead, and cyanide complexes. Achievable reduction limits are dependent on a variety of factors including plant size, flow rate and the nature of the process considered. The ultimate goal is a zero discharge policy and complete control of the toxic metals [5].

As trace elements, some heavy-metals are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy-metal poisoning could result from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain. Heavy-metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over

time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down or excreted. Heavy-metals can enter a water supply by industrial and consumer waste, or from acidic rain breaking down soils and releasing heavy-metals into streams, lakes, rivers, and groundwater. The following sections outline some metal elements that may be of concern to the hydromet process, their key toxicity thresholds, and the potential effects if exposure occurs.

Cadmium

Cadmium is a highly toxic metal and can cause serious damage to humans and the environment [18]. The World Health Organization has recommended that the permissible intake of cadmium should not exceed 0.4 to 0.5 mg per week or 0.057 to 0.071 mg/day. A maximum acceptable concentration of 0.005 mg/L (5 $\mu\text{g/L}$) for cadmium in drinking water has been established on the basis of health considerations [19]. As outlined by the Canadian Environmental Quality Guidelines updated in 2002, the concentration of cadmium in freshwater and marine environments is 0.012 $\mu\text{g/L}$ and 0.12 $\mu\text{g/L}$ respectively [20].

Chromium

Chromium exists in the aqueous environment in either the hexavalent or trivalent form [18]. A maximum concentration of 0.05 mg/L (50 $\mu\text{g/L}$) for chromium in drinking water has been established on the basis of health considerations [21]. Trivalent chromium is the most naturally occurring state of chromium and is not considered to be toxic unless present in raw water where it may be oxidized to hexavalent chromium during chlorination. Chromium enters the body and becomes immobilized as trivalent form and accumulates leading to increased chances of various forms of cancer [18].

Copper

For humans, copper is an essential element and the body can regulate its level homeostatically, but large, acute doses can have a harmful, sometimes fatal, effect [18]. Copper in drinking water should be limited to ≤ 1.0 mg/L [19].

Cobalt

Cobalt is not generally included in lists of heavy-metals which are harmful to the environment. However, it is known that cobalt can have diverse effects at high concentrations [18].

Lead

Lead is toxic to human, aquatic fauna, and livestock. In the aquatic environment it exists in the inorganic, divalent state or in the tetravalent state. As outlined by the Canadian Environmental Quality Guidelines updated in 2002, the concentration of lead in freshwater is 1-7 $\mu\text{g/L}$ depending on the concentration of calcium carbonate in the stream [20].

Nickel

Nickel does not have a serious effect on humans but has an appreciable phytotoxicity [18]. The concentration limits in freshwater is between 25 and 150 $\mu\text{g/L}$ depending on the concentration of calcium carbonate in the stream [20].

Zinc

Zinc is not perceived to pose a serious risk to human health, the limit in drinking water is 5 mg/l [18].

2.6 Separation Criteria

In order for any waste treatment technology to be a viable process in the mineral processing industry it must comply with a number of standards. The most important criteria when considering effluent treatments is related to cost effectiveness and the resulting imposed environmental impacts [3]. The effluent clean-up process should be:

- compatible with the existing unit operations
- cost effective (i.e. not adding to the overall production costs)
- flexible in handling changes in quality and quantity of feed
- reliable to operate in continuous mode
- robust to operate with minimal supervision and maintenance
- selective in the removal of the metals that are of interest
- simple to operate to minimize the need for skilled operators

Separation technologies are developed for both processing and environmental applications. The effluent treatment process has to be capable of handling a variety of feed streams that may vary in quantity and quality.

Chapter 3

Ion-Exchange

“Every year thousands of pounds of recoverable metal values are allowed to go to waste” [22]. Not only is this an economic oversight, but it also contributes to the damage of the environment. One solution that is being used to improve how waste is managed in industrial facilities is the incorporation of ion-exchangers into process design to recover metals and water, and to reduce pollution. Ion-exchangers are a potential application for recovery and purification of metals and offer economic and technical advantages in treating dilute solutions.

The goal of any treatment strategy is to obtain the maximum product reclamation from the effluent and to reduce the concentration levels below the allowable limits imposed by legislation. The overall economic viability of any treatment process depends on the value of the recovered metals and the operating costs that are involved in obtaining these metals [26].

Ion-exchange is a special case of adsorption. It is a purification process that removes and separates ions in solution. It is a reversible interaction of ions between the resin material and ions in a solution in which no permanent changes occur to the

resin structure. Its use has been established in a number of industrial applications, including the treatment of wastewater, and has been proven to be successful due to its ability to remove trace impurities from effluents.

3.1 Fundamentals

The law of electro-neutrality governs the operation of the ion-exchange process. It dictates that ions of opposite charge will be attracted to one another, and that the total number of ions leaving the solution will equal the number entering the solution [23, 24, 25].

The basic ion-exchange process includes passing a liquid stream over a fixed bed which absorbs the desired ions from the stream. Once the fixed bed becomes saturated the flow stops and the absorbed ions are recovered through desorption so that the fixed bed can be reused.

3.1.1 Equilibrium Conditions

The equilibrium between the concentration of a solute in the liquid phase and the concentration on the solid resin can be expressed in terms of adsorption isotherms. Data that follows a linear trend can be expressed in the following manner:

$$q = Kc \tag{3.1}$$

where q is the kg of adsorbate (solute)/ kg adsorbent (solid), c is the kg of adsorbate/ m^3 of fluid, and K is determined experimentally.

If the data follows the Freundlich trend (non-linear) then the isotherm can be estimated by using the following relationship:

$$q = Kc^{(1/n_c)} \quad (3.2)$$

where K and n_c are experimental constants.

A Freundlich isotherm can then be represented by plotting the capacity of the media for the component (C_a/X) versus the equilibrium concentration (C_f) as shown in Figure 3.1, where X is the mass of the separation media. The shape of the curve indicates the feasibility of the separation media in achieving the desired separation under the test conditions.

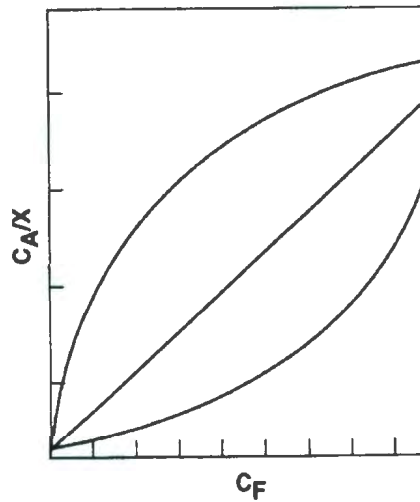


Figure 3.1: Adsorption Isotherm using Freundlich Trend [28]

Another relationship for estimating equilibrium isotherms is the theoretically based Langmuir model:

$$q = \frac{q_o c}{K + c} \quad (3.3)$$

where q_o is the kg adsorbate/ kg solid[50].

Generally, adsorption processes demonstrate that an increase in temperature decreases the amount of adsorbent (metal of interest) that is absorbed by the resin. This means that desorption (release of metals) can be obtained by raising the temperature. Knowledge of an adsorption isotherm is important in the characterization of the system and will allow the system to be designed for maximum resin efficiency.

The ion-exchange process can also be modeled as flow through a porous media. This model is more complicated and requires a more in depth study than simply having a stream of fluid pass over a fixed bed. In this process, mass-transfer resistances are an important consideration and the process is generally considered unsteady. The efficiency of the process is governed by the dynamics of the system and equilibrium considerations.

The concentration of the solute in the liquid phase and the solid in the adsorbent phase changes with time and position in the porous media. As time progresses there will be a dynamic concentration profile in the porous media with a distinct mass-transfer zone. The difference in concentration is a driving force for mass-transfer. Once the breakpoint is reached, where the concentration propagates completely through the porous media, the concentration at the exit reaches the feed concentration very rapidly.

Changing the resin matrix shape, or the contact duration will have an effect on the breakthrough curve. Parameters such as average resin bead size, feed flow rate,

resin bed depth, and the operating temperature all play a role in developing the breakthrough curve. Figure 3.2 shows a sample breakthrough curve depicting the concentration of a target ion at the outlet versus time.

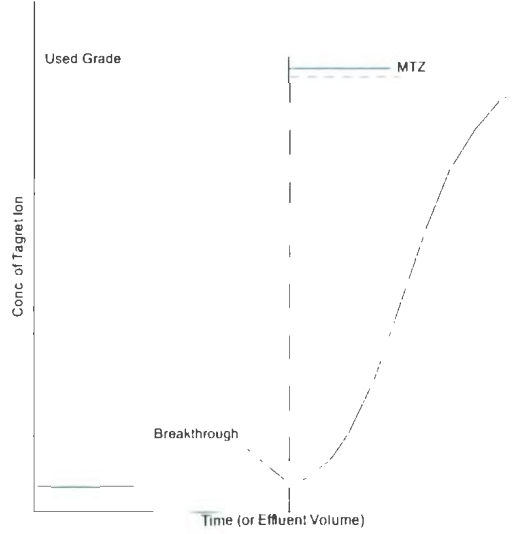
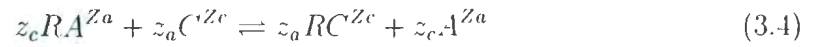


Figure 3.2: Sample Breakthrough Curve for Ion Exchange Process [29]

To maintain the law of electro-neutrality, the resin must release ions in order to have available receptive zones for exchange with the effluent. The following chemical reaction is an example of this ion-exchange balance equation:



where R represents the insoluble material with binding sites (resin), A is the counter ion (A and C are exchanged). The charged ions are in solution and the resin is the solid. The left side of the equation represents the effluent solution whereas the right side represents the treated solution.

Equilibrium isotherms have been developed using mass action laws to calculate the

equilibrium condition. In the case of the previous ion-exchange reaction, Equation 3.4, the selectivity coefficient for A/C ion exchange is:

$$K_{C/A} = \frac{[RC]^{Z_a}[A]^{Z_c}}{[C]^{Z_a}[RA]^{Z_c}} \quad (3.5)$$

Equilibrium constants have been tabulated for various types of ion-exchange resins in order to facilitate ion-exchange design. The selectivity coefficient is dependent on concentration of both elements, the total ionic strength of the solution, and the temperature (at a constant pressure).

A number of factors affect the distribution of metals between the solution that is being treated and the solid ion-exchange resin. The distribution coefficient is used to measure the metal distribution for ion-exchange:

$$K_D = \frac{[RC]}{[C]} \quad (3.6)$$

measured in ml/g. This equation is valid when the ion R is present at trace levels (i.e. $[C] \ll [A]$).

Every exchanger has a maximum amount of charged sites per gram of resin. This value is the theoretical specific capacity, Q_c , measured in meq/g. The capacity is identical to the charge density due to ionogenic groups [30].

3.1.2 Concentration Profiles and Breakthrough Curves

The modeling of an ion-exchange process is similar to an adsorption process. The rate of ion-exchange depends on the transfer of ions from the fluid to the resin surface,

diffusion of the ions through the pores of the solid to the surface, and the exchange of the ions at the surface back to the solution. The concentration profiles in packed beds are also similar to adsorption. The main part of the ion-exchange process occurs in a narrow mass-transfer zone. As the mass-transfer zone proceeds down the column, the height of the column becomes constant because the ions in the fluid tend to be more attracted to the resin rather than remaining in solution. The constant height can then be used to scale up the model.

The scale-up methods are necessary because of the uncertainty involved with theoretical prediction due to the complicated flow patterns through the packed bed. Small scale laboratory experiments are necessary. The total stoichiometric capacity of the packed bed is the area under the breakthrough curve, which can be found using the following equation:

$$t_t = \int_0^{\infty} (1 - c/c_o) dt \quad (3.7)$$

where t_t is the time equivalent to the total capacity.

The usable capacity occurs until the breakthrough point t_b :

$$t_u = \int_0^{t_b} (1 - c/c_o) dt \quad (3.8)$$

For a total bed length of H_T the length of bed used up to the break point is H_B :

$$H_B = (t_u/t_t)H_T \quad (3.9)$$

This leads to the determination of the unused bed or the length of the mass-transfer

section in meters (m):

$$H_{UNB} = (1 - t_u/t_t)H_T \quad (3.10)$$

For scale up, the experimental value of H_{UNB} is measured and H_B is determined based on the desired capacity at the break point. The total column length becomes:

$$H_T = H_{UNB} + H_B \quad (3.11)$$

The above equations are based on binary exchange. Thermodynamic formulation of binary cation or anion-exchange equilibrium is simple compared to multi-component equilibrium systems, which become increasingly more complicated as the number of exchanging components are increased [31].

3.2 Ion-Exchange Process

The ion-exchange process requires a certain amount of basic equipment [23, 24, 25]. A shell is necessary to contain the resin and house the flow of the dilute aqueous solution. A typical container size is 1-7 ft in diameter and 4-12 ft in height, however this is a function of process facility capacity and cycle times. The size of the exchanger is normally left up to the discretion of the engineer to optimize the diameter of the unit (for flow distribution), the height of the unit (for pressure drop), and the thickness of the resin. Secondly, the resin must be supported. This is accomplished partly using flow distribution devices and partly by graded coal, gravel, porous metal, or ceramic plate. The third component of the unit is the distribution devices themselves,

which are used to distribute the flow uniformly over the resin. Fourth, the resin will tend to swell during use so it is a necessary consideration in the design of the unit. Backwash space is necessary for the reclamation of the resin when it is expanded to flush out all lodged particles. Finally, there is a need for inlet and outlet lines with instrumentation for trouble free operation in order to control the flow and back pressure.

The process of ion-exchange takes place in four main steps: service, backwash, regeneration, and rinse [32, 33]. Figure 3.3 shows a simplified diagram of a typical ion-exchange operation.

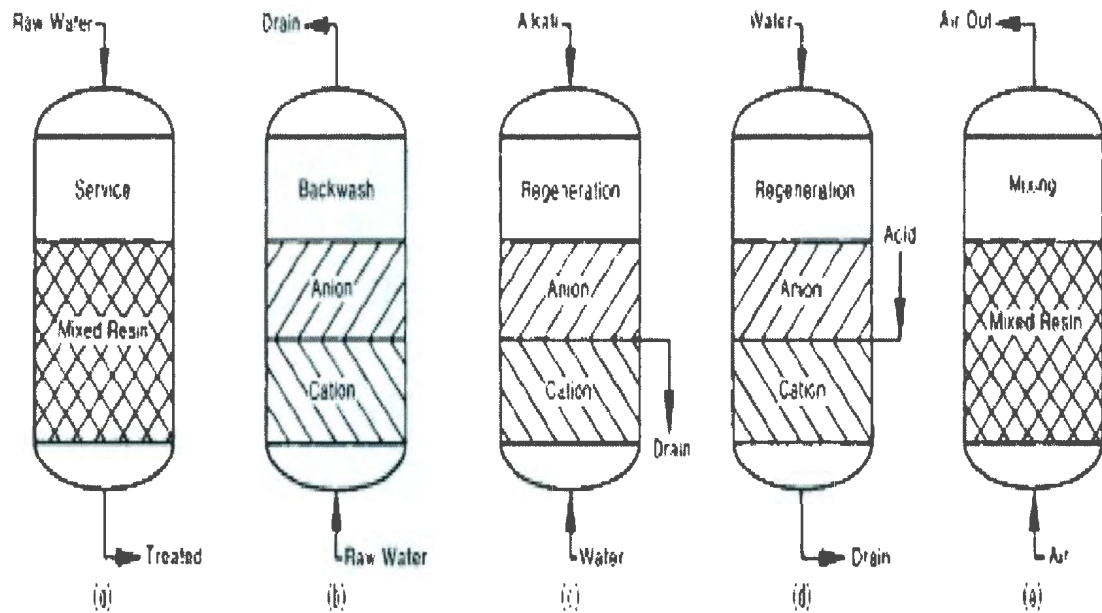


Figure 3.3: Sample Ion-Exchange Operation a) Service period, b) Backwash period, c) Caustic regeneration, d) Acid regeneration, e) Resin mixing [51]

3.2.1 Service

The feed solution to be treated is passed through the ion-exchange resin and mobile ions in the solution are exchanged for ions attached to the resin. This continues until the resin has absorbed the maximum amount of ions from the solution. The ions move from the bulk of the solution, through the laminar film, and into the pores of the resin.

3.2.2 Backwash

The backwash step is required for maintenance of the ion-exchange system. It is required after the initial installation and following each run. The purpose of this stage is to remove any particles (such as silt, dirt, insoluble matter, or excess resin) which may exist within the ion-exchange bed. Performing this step will keep the ion-exchange process operating at maximum efficiency by extending the life of the exchange resin and ensuring proper flow characteristics.

Resin manufacturers recommend removing suspended solids to a negligible level prior to the ion-exchange operation since the solids will gradually accumulate within the ion-exchange resin bed. Solid accumulation can lead to poor distribution of the water and regenerants within the resin bed and thus leading to increased pressure loss [34].

3.2.3 Regeneration

The resin bed is brought in contact with the regenerant solution. The fixed ions diffuse outward through the laminar film of the resin and back into the bulk of the solution. The ions fixed to the resin are removed and are replaced with hydroxyl

(anion-exchanger) or hydrogen (cation-exchanger) ions.

It is possible for the resins to experience swelling, shrinkage, or both, during the regeneration stage. An additional backwash step may be required to ensure the full life span of the resin and to prevent channeling, resin compression, or both. The frequency of the regeneration and backwash steps vary depending on the volume of resin in the column as well as the quantity of heavy-metals and other ionized compounds present in the wastewater stream.

Ion-exchange regeneration technologies have evolved over the years. As shown in Figure 3.4 industries have the option of using either the co-flow or counter-flow regeneration scheme.

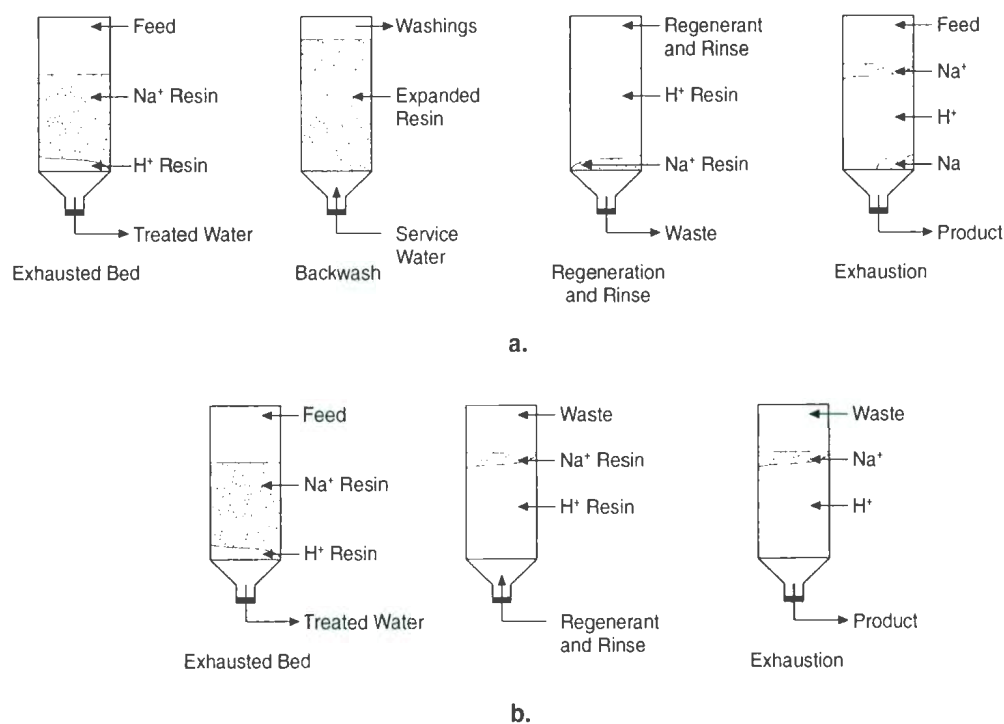


Figure 3.4: Ion-Exchange Operation (a) co- and (b) counter-current-flow regeneration (H^+ form cation resin; Na^+ removal) [35]

Co-current Regeneration

In this process, the resin is regenerated in the same direction as the service flow. The vessel has extra space to allow expansion of the resin bed when backwashing takes place.

Counter-Current Regeneration

Regenerant is in the opposite direction of the service flow. In order to obtain low leakage levels, the contaminating ions must be kept from the effluent end of the column during regeneration and rinse stages. In this process, frequency of backwash is minimized. Counter-current regeneration system have reduced chemical costs, improved water quality, and have ended up with a final product that has less waste volumes as compared to the co-flow technique [35]. Advantages such as increased productivity, smaller vessel sizes, increased regeneration time, and fewer mechanical failures have been recognized.

Figure 3.4 demonstrates the leakage that takes place in the two systems. As can be seen, leakage in counter-flow regeneration is reduced since the resin bed is mostly in the regenerated form at the bottom of the vessel [35].

3.2.4 Rinsing

In this step all the excess regenerant solution is removed and the system is prepared for service.

3.3 Types of Ion-Exchange Units

In the ion-exchange process, certain components of the entering fluid are converted into insoluble rigid particles that are suspended in a vessel (batch-type operation), packed in a column (column-type operation), or in a fluidized environment (moving-bed-type operation). These rigid particles can then be removed for further processing and recovery of the metals of interest [36].

3.3.1 Batch Operation

The resin and solution are mixed in a tank until the conditions of equilibrium are achieved, after which the resin is separated from the solution. This process is limited by the selectivity of the resin under the conditions of equilibrium [32].

The batch ion-exchange units are limited by the selectivity for the ion in solution. Disadvantages to this method include inefficient use of regeneration chemicals and increased tendencies to become clogged with residue which can lead to decreased separation ability [37].

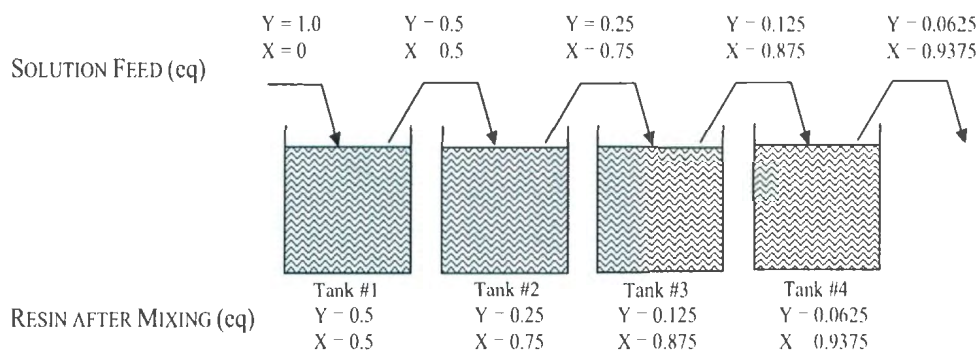
3.3.2 Column Operation

The column-type ion-exchange unit is equivalent to multiple batch operations in series. Types include downflow, upflow, and counter-flow. Most types used in industry are downflow where the feed and the resin pass through the resin bed. These units are less expensive in terms of equipment needed but uses regenerant chemicals less efficiently, has higher leakage concentrations, and cannot achieve as high a product concentration in the regenerant. The upflow system is where the feed and resin are

raised through a bed, and the counter-flow operation consists of the feed flowing down from the top and the resin flowing from the bottom to the top.

With the use of a column ion-exchange unit, separations are possible despite poor selectivity for the ion being removed. This theory is explained by a simplified diagram of the column-type operation, Figure 3.5. Each tank contains 1 equivalent (eq) of resin in the X ion form. A solution feed containing 1 eq of Y ions is sent into the first tank. Assuming that the resin has an equal preference for ions X and Y, once equilibrium is reached the solution phase and the resin in the first tank will contain 0.5 eq of X and Y. In the second stage, the solution exiting tank 1 enters tank 2, which also contains 1 eq of resin in the X form. Following equilibrium, the exiting solution and the resin will contain 0.25 eq of Y ion and 0.75 eq of the X ion. The third and fourth tanks follow the same procedure, and the exiting solution would reduce to a value of 0.0625 in the Y ion form and 0.9375 in the X ion form. This simplified example shows that through the use of sufficient stages the Y ion concentration can be reduced to a desired level. After a feed solution passes through the system, the resin becomes exhausted and is not capable of further ion-exchange at which time the resin is regenerated.

An option with the column operation is to have the ion-exchangers set up in a lead-lag format where the lead column is where most of the metal is removed and passed onto the second column where any residual metal is removed. Once the first column becomes saturated and breakthrough occurs, the higher metal levels can be passed on to the second column. The lead can then be regenerated while the lag becomes saturated.



NOTE: Each tank initially contains 1 cq of resin in the X ion form.

Figure 3.5: Concentration Reduction of Y ion using a Column Type Ion-Exchange Unit [32]

3.3.3 Moving Bed Operation

Moving bed ion-exchange operations are used where the resin and the solution flow through the system. The resin is contacted counter-currently with the exhausted stream and the regeneration stream. The advantages of this operation is that there is a continuous product of uniform quantity at less space, capital, and labor. The problem with the system involves the complexity of the design. Fluidized-bed ion-exchange systems have been used in the treatment of solutions containing suspended solids. The ion-exchange system splits a liquid effluent into two currents, one being more concentrated and the other more depleted of a given component. The system operates in a semi-continuous way using two multi-stage columns, one for loading and the other for elution of the resin [37].

Figure 3.6 displays a typical fluidized-bed ion-exchange unit. The columns are divided into four stages and each stage is separated by punched plates. At the base of the columns are two collection tanks that are separated from the columns by a control

valve. When this valve is opened, resin and liquid in the 1st stage of the column falls into the tanks and the resin in the other stages drop down one level. In the continuous operating mode, load and elution occur simultaneously. There is an improved mass-transfer between the liquid and the solid phases. The counter-current operation mode improves the efficiency in both the loading and the regeneration columns.

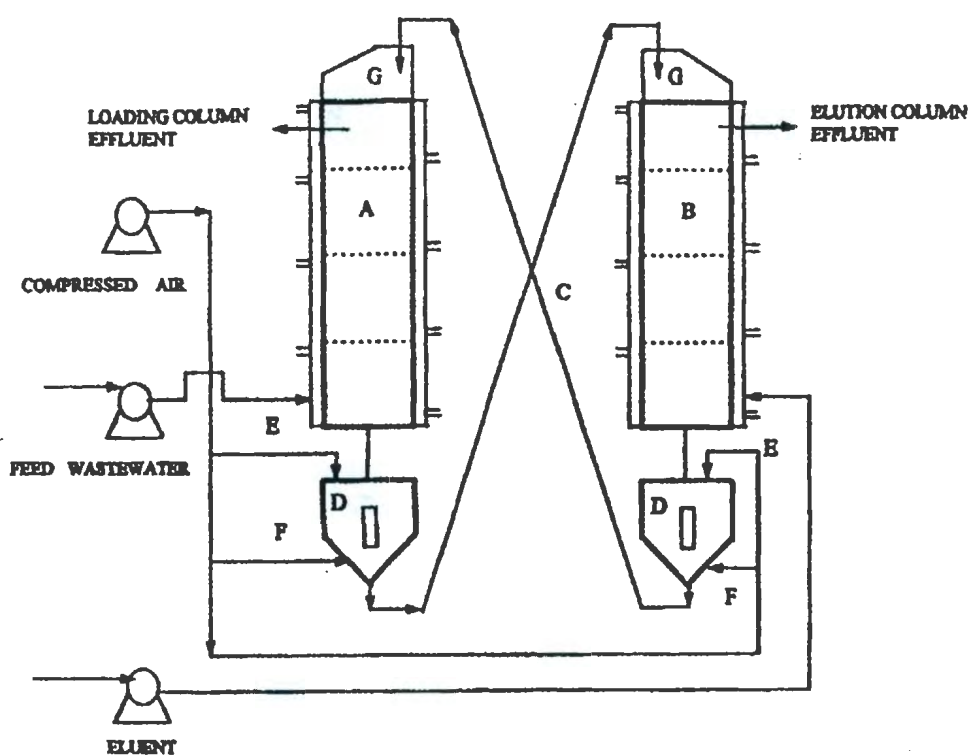


Figure 3.6: Simplified Moving-Bed Ion-Exchange Unit [37]

3.4 Resins

An ion-exchange resin is defined as a polymer that contains fixed electrically charged sites where one ion on the resin may replace one ion in solution [38]. The literature

available in the area of ion-exchange resins is extensive demonstrating the multitude of resins that are commercially available for the selective removal of a wide range of metals. The advancement of technology has enabled resins to be created with superior selectivity of valuable species compared to most other absorbents [39]. Ion-exchangers can be organic, inorganic, or both, and can consist of synthetic or natural materials.

3.4.1 Inorganic Resins

Zeolites, often referred to as molecular sieves, are microporous crystalline solids that contain well-defined structures[40]. The framework consist of interlocking tetrahedrons of SiO_4 and AlO_4 . Zeolites are typically anionic, and charge compensating cations populate the pores to maintain electro-neutrality [40].

The shape-selective properties of zeolites allow for selective adsorption of certain molecules, while excluding others. Zeolites have large vacant spaces in their structure to allow for large cations to be readily exchanged for other types of metals in an aqueous solution. Some minerals of the zeolite group allow for the spaces to become interconnected and form long wide channels of varying sizes which allow for easy movement of molecules into and out of voids [41].

Zeolities are a simple and inexpensive solution to the treatment of industrial wastewater. They have proven to successfully remove heavy-metals. Natural zeolites have been used for the removal of heavy-metal cations such as copper (Cu^{2+}), cadmium (Cd^{2+}), zinc (Zn^{2+}), nickel (Ni^{2+}), and lead (Pb^{2+}) [42].

Faghihian et al. (1999) [43] describe the use of natural zeolites (specifically clinoptilolite) for the removal of heavy-metal ions in an ion-exchange process. This paper focuses on its use for the removal of cesium (Cs^+), Ni^{2+} , strontium (Sr^{2+}), Cd^{2+} , bar-

ium (Ba^{2+}), and Pb^{2+} from wastewater. It was found that the effective pH range for metal removal was between 3.5 and 8.0 even with the presence of alkali or alkaline-earth cations. It was determined that clinoptilolite is a suitable ion-exchanger to decrease the heavy-metal content of weakly alkaline wastewater from several thousand ppm down to 10-100 ppm [44]. Clinoptilolite and chabazite have been used for the separation of transition metals from mixed metal contaminant effluents [45].

It has been found that the functionality of natural ion-exchangers has limited use in some specific industrial applications. The chemical resistance offered by these types of resins is sufficient for some cases, but at times their microbiological sensitivities restrict their use in the hydrometallurgical industry [30].

3.4.2 Organic Resins

Organic resins with a cross-linked hydrocarbon matrix and derivatized with an inorganic group are common ion-exchange materials used in a number of industrial applications. Some commercial resins consist of a styrene-divinylbenzene structure which is based on copolymers of a vinyl compound (styrene) and a cross-linking agent divinylbenzene (DVB) which can range from 4% to 16% [38]. This structure provides resistance against physical stress and is stable at relatively high temperatures over a large pH range [30].

The use of synthetically produced resins is commonly encountered in industry due to its ability to be customized to each individual application to target specific metals that are of interest in the effluent stream. Each resin has a maximum number of available mobile sites capable of exchanging ions within the fluid medium [32].

Cationic or anionic exchange is determined by the functional group that is added to

the resin. Cation-exchangers have positively charged mobile ions that are available for exchange, while anion-exchangers have negatively charged ions for exchange. By entering the structure and attaching to the surface area of the resin, these functional groups determine the chemical behavior of the resin. Resins can be classified into strong or weak acid cation-exchangers, and strong or weak base anion-exchangers.

Figure 3.7 shows the exchange capacity of weak acid cation and weak base anion resins as a function of pH. As shown, the exchange capacity for the weak base anion resin is limited over a pH of 7.0, while the weak acid cation resin has a limited capacity under a pH of 7.0.

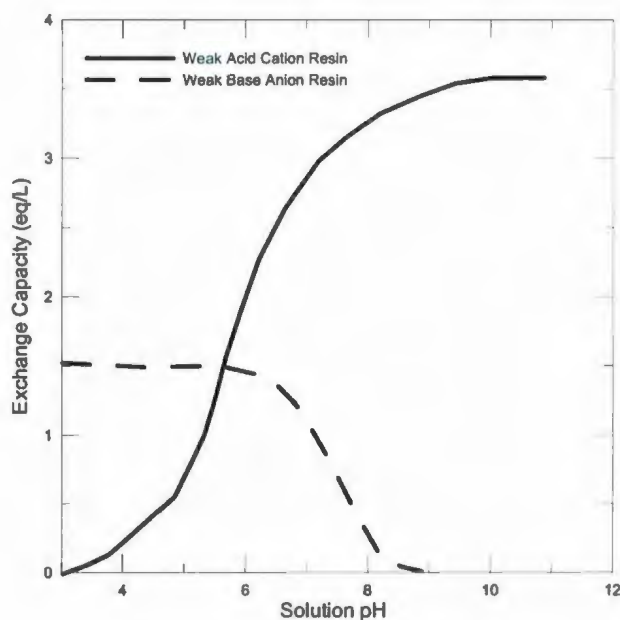


Figure 3.7: Exchange Capacity vs. pH for Weak Acid and Base Resins[32]

Typical regeneration capacities of commercially available cation and anion resins are shown in Figure 3.8. As shown, the capacities are influenced by the quantity of acid or base used to regenerate the resin. Weak acid and weak base systems are more efficiently regenerated and their capacities increase linearly with regenerant amounts.

The weak and strong base anion resins were calculated using $\text{lb NaOH}/ft^3$ (of resin) while the weak and strong acid cation used $\text{lb HCl}/ft^3$ (of resin). Weak ionized resins require only slightly greater than stoichiometric chemical doses for complete regeneration while for the strong acid or strong base resins, efficiency of the regenerant chemicals is a primary concern.

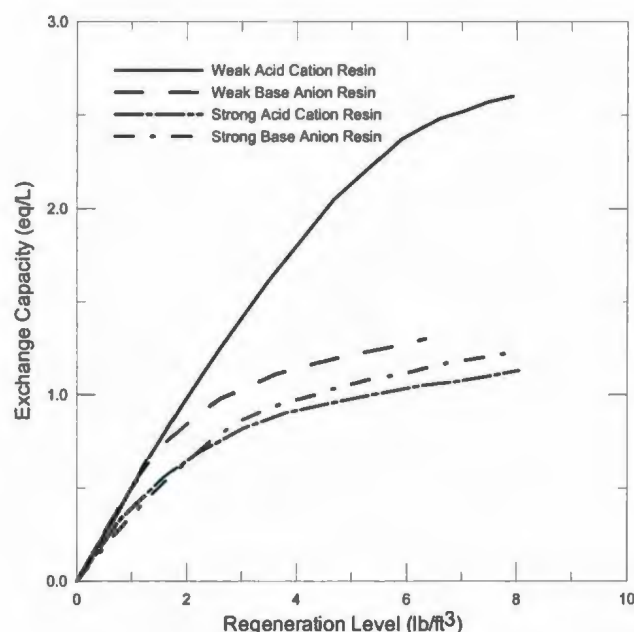


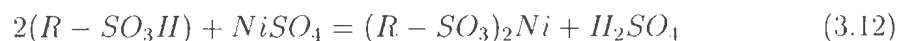
Figure 3.8: Regeneration Capacities of Commercial Resins for Ion Exchange Process [32]

Strong Acid Cation Resin

Strong acid cation resins are ionized in both the acid ($R - SO_3H$) and salt ($R - SO_3Na$) forms. Both the hydrogen and sodium forms of the strong acid are highly detachable and the Na^+ and H^+ ions are available for exchange. After the exchange is complete, the resin can be regenerated back to the hydrogen form using a strong acid solution, or back to the sodium form using a sodium chloride solution. In the hydrogen

form, these resins would be used for complete deionization whereas in the sodium form water softening can be achieved. It has also been used in special applications such as two-step metal-cyanide recovery treatment of acidic copper or zinc solutions [30].

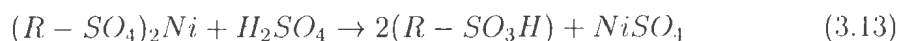
Regeneration with hydrochloric acid (HCl) would result in a highly concentrated nickel chloride (NiCl) solution [32]. Resins exchange hydrogen ions H^+ for positively charged ions such as nickel, copper, and sodium. Equation 3.12 shows an example of a strong acid cation resin that exchanges the H^+ ions on the resin for Ni^{2+} ions in solution:



where R is the organic portion of the resin and SO_3 is the immobile portion of the ion active group. For every nickel ion with +2 valence, two resin sites are required for equilibrium. In the case of trivalent ions, three resin sites are necessary for the reaction to take place. The degree that the reaction will proceed to the right depends on the resins preference or selectivity for the nickel ions as compared to the hydrogen ions [32].

In general, most resins are moderately resistant to oxidization, insoluble in solvents, and are hydrophilic. Also, most waste treatment systems operate at 50-80% chemical efficiency due to foulants and precipitates that get into the resin bed [46] .

Regeneration occurs by contacting the resin with a concentrated solution of sulfuric acid (H_2SO_4). The following reaction takes place:

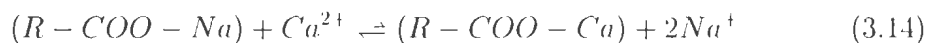


A strong acidic cation-exchanger will successfully remove heavy-metal ions, however it may also remove harmless cations such as sodium, calcium and magnesium. These background ions cause problems when they are present in concentrations greater than the heavy-metal content in the waste stream since they compete with the heavy-metals for exchange sites on the resin.

Weak Acid Cation Resin

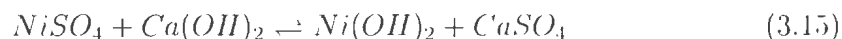
The ionizable group in this type of resin is a carboxylic acid (COOH). Weak acids have a high affinity for hydrogen ions therefore regeneration back to the hydrogen form takes place with reduced amounts of acid making it more economically feasible. The degree of dissociation of a weak acid cation resin has a limited capacity at pH values lower than 6.0, as shown in Figure 3.7. This resin structure is therefore not recommended for de-ionizing acidic metal finishing wastewater [32]. Weak acid cation resins are very selective to divalent cations, particularly copper and nickel, which make them applicable for removal of metals from wastewater [46]. Their use is very effective in neutral to alkaline pH environments. Many metals form hydroxide complexes when the pH is high, thus by keeping the pH in the 6-8 range prevents precipitation of the metals which leads to fouling of the resin [46].

An example of a weak acid ion-exchange resin that uses the carboxylic acid radical in the sodium form is R-COO-Na , shown in Equation 3.14. As metal ions such as magnesium (Mg), calcium (Ca), and copper (Cu) pass through the resin they are exchanged for the Na^+ ions. Sodium chloride (NaCl) can be used to regenerate the resin.



Strong Base Anion Resin

This type of resin is highly ionized and is used over a wide range of pH values. In some situations this resin will react with anions in solution and will convert an acid into pure water. The hydroxyl ion (OH^-) is used for the water deionization process. Regeneration back into the hydroxide form takes place with the use of sodium hydroxide (NaOH). Applications include the removal of anionic metal complexes from acidic waters like $ZnCl_4^{2-}$ in spent pickle solutions or Cr(VI) in rinse water after chromating [30]. Hydroxyl ions are exchanged for negatively charged ions such as sulfates, chromates, and chlorides. An example follows:



The nickel ions (Ni^{2+}) of the nickel sulfate ($NiSO_4$) are exchanged for the calcium ions (Ca^{2+}) of the calcium hydroxide ($Ca(OH)_2$).

Weak Base Anion Resin

This type of resin is useful for a small range of pH values, and has minimum exchange rates over a pH of 7.0, as shown in Figure 3.7.

Chelating Resins

Chelating resins are macroporous polystyrene based resins derivatized with iminodiacetic acid groups. These types of resins are similar to weak acid cation resins, but are highly selective toward heavy-metal ions present in waste streams. The selectivity of the resin for a metal depends on the concentration and presence of other metals, and the pH [47].

An iminodiacetic acid resin is useful in the removal of metals when a chelate such as ammonia or ethylenediaminetetraacetate (EDTA) is present. A chelate is a chemical compound that is composed of a metal ion and a chelating agent [48]. Figure 3.9 shows an EDTA chelating agent which can form 4-6 bonds with a metal ion. It is capable of forming chelates with both the transition-metal ions and the main-group ions [48]. Due to their capability of attaching multiple bonds to the metal of interest, the chelates tend to be more stable than complexes formed with monodentate ligands. The increased stability can be explained by the bonds that are formed which usually have both covalent and ionic characteristics [30].

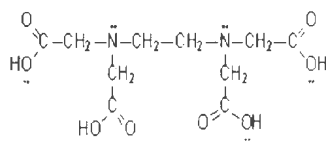


Figure 3.9: Molecular Formula of Ethylenediaminetetraacetic Acid (EDTA)[48]

A chelating resin exists in both the sodium and hydrogen forms, but exhibits greater selectivity for heavy-metals in its sodium form. It is possible to convert the resin back into its hydrogen form by adding slightly more than stoichiometric amounts of acid or base since heavy-metal complexes are less stable in low pH environments [32].

A chelating resin is used in situations where there is a large amount of background ions such as magnesium, calcium, or sodium that would reduce the efficiency of other available resin types. In most waste streams the concentration of various metals in solution are close to one another and therefore a resin with a high selectivity toward a particular metal is necessary for effective separation to take place.

Chelating resins are used in a variety of processes; two examples are to lower the heavy-metal concentration in the effluent from a hydroxide treatment process, and to remove toxic heavy-metal cations from wastewater containing a high concentration of nontoxic, multivalent cations. One of the main downfalls of the use of chelating ligands is the high cost that corresponds to its use [32]. This type of resin requires a greater amount of regenerant solution in the regeneration stage of the process.

Chelating resins have some qualities that make them ideal for removal of dilute metals from waste streams, but they also have some negative qualities. The cost of utilizing a chelating resin is very high compared to conventional methods. The kinetics of a chelating resin is also much slower, and therefore requires larger volumes of the resin as compared to conventional resins [30].

3.4.3 Selectivity of Ion-Exchange Resins

Table 3.1 gives the selectivity of strong acid and strong base ion-exchange resins for various ionic compounds. As indicated, strong acid resins have a preference for nickel over hydrogen. The higher the degree of preference a resin has for an ion, the greater the exchange efficiency of removal of that ion from solution. Also, greater preference for a particular ion causes an increase in the consumption of chemicals during the regeneration process.

Table 3.1: Selectivity of ion-exchange resins in decreasing order [32]

Strong acid cation exchanger	Strong base anion exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate
Ammonia Sodium	
Hydrogen	

Table 3.2 shows the selectivity coefficients for a commercially available chelating resin for different metals as compared to calcium ions at three pH values. At pH = 4, the preference for copper is 2300 times more than that for calcium, i.e. in a solution containing equal amounts of copper and calcium ions the molar concentration of the copper ions on the resin will be 2300 times the concentration of calcium ions. The affinity for a metal can be altered by changing the pH of the solution [47].

3.4.4 Effectiveness of Ion-Exchange

There are a number of factors that contribute to the effectiveness of an ion-exchange process. Each property has an effect on the productivity and the quality of the resulting fluid concentration that is observed during operation. Density, mechanical resistance, grain size, capacity, and equilibrium rate determine the functionality of a particular ion-exchanger in any industrial application.

Table 3.2: Selectivity Coefficients of Serdolit Chelate Resin [47]

pH=2		pH=4		pH=9	
Metal Ion	K_{Ca}^M	Metal Ion	K_{Ca}^M	Metal Ion	K_{Ca}^M
Fe^{+3}	325000	Hg^{+2}	2800	Ni^{+2}	30
Cu^{+2}	130000	Cu^{+2}	2300	Cd^{+2}	14
Hg^{+2}	> 43000	Pb^{+2}	1200	Cu^{+2}	10
Au^{+3}	> 8100	Ni^{+2}	57	Zn^{+2}	57
Ag^{+}	4600	Zn^{+2}	17	Ca^{+2}	17
Ni^{+2}	3200	Cd^{+2}	15		
Cd^{+2}	620	Co^{+2}	6.7		
Fe^{+2}	190	Fe^{+2}	4.0		
Mn^{+2}	120	Mn^{+2}	1.2		
Zn^{+2}	120	Ca^{+2}	1.0		
Al^{+3}	50				
Mg^{+2}	20				
Ca^{+2}	1.0				

Density

In the ion-exchange process, water diffuses into the structure, causing it to swell until the osmotic forces are satisfied. The density of the water swollen resin is determined by the type of counter-ion present, swelling capacity of the resin (as defined by the nature of its polymer structure), and the degree of cross linkage.

The effectiveness of a particular ion-exchange resin is determined by cross-linkage, which is based on the proportion of different monomers used in the polymerization step. The lower the cross-linkage the higher the moisture content of the resin as shown in Figure 3.10.

Mechanical Resistance

Mechanical resistance varies with the structure of the resin. An important factor to consider during the resin selection stage is that air dried resins can be destroyed with

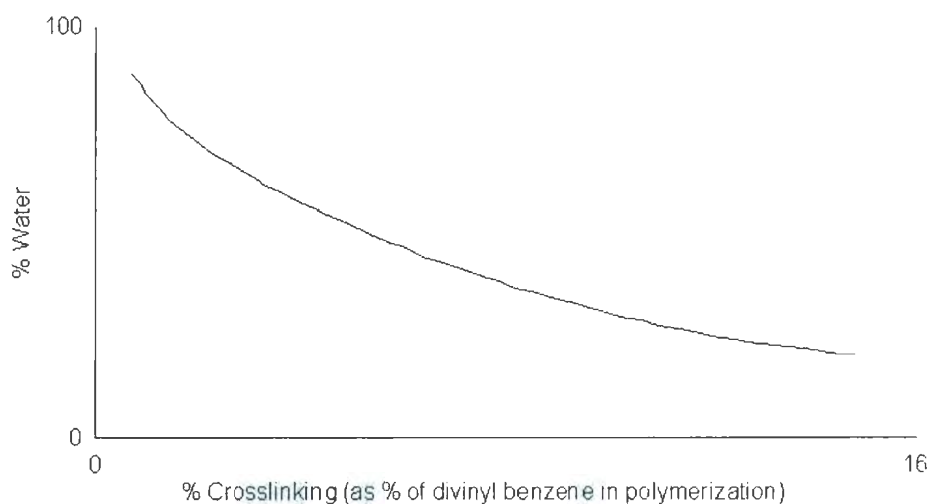


Figure 3.10: Conceptual Linear Plot of Moisture Content vs Crosslinkage [38]

a certain amount of friction.

Grain Size

The size of resin particles is controlled during the polymerization step through the use of various mesh sizes to obtain uniform particle diameters. The particle size influences the time to reach equilibrium conditions. There are two types of diffusion that take place in an ion-exchange system. Film diffusion is the movement of ions from the surrounding solution to the surface of the ion-exchange particle. Internal diffusion is the movement of ions from the surface to the interior of an ion-exchange particle. Film diffusion is normally the controlling reaction in dilute solutions whereas internal diffusion is controlling more concentrated solutions. A fine mesh particle presents more surface area for film diffusion and contains less internal volume through which an ion must diffuse, therefore reducing the time required to reach equilibrium.

Capacity

Resin capacity is measured in terms of equivalents available for exchange per unit volume (eq/L) of wet resin, or unit weight of dry and wet resin (eq/g). An equivalent is defined as follows:

$$\text{Equivalent}(eq) = \frac{\text{MolecularWeight}(g/mol)}{\text{ElectricalCharge}} \quad (3.16)$$

Figure 3.11 shows the typical capacities for resins as a function of cross-linkage.

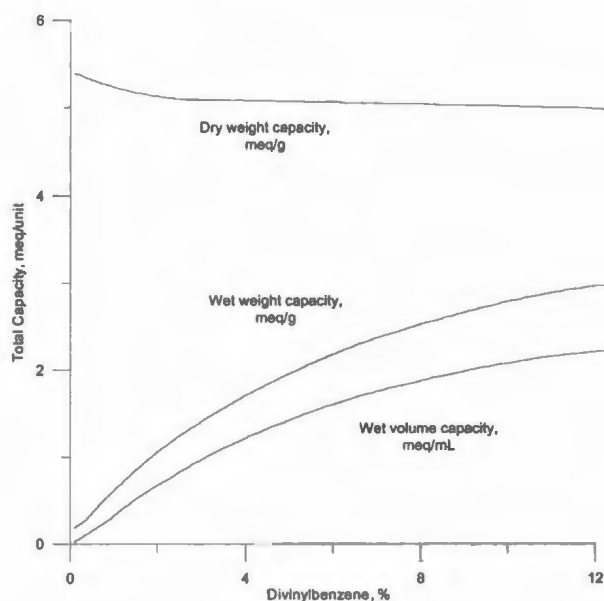


Figure 3.11: Moisture Content vs Cross linkage for Divinyl benzene adsorption[35]

The capacity of a resin measured on a dry basis drops slightly as cross-linkage is increased. This is explained by the increased resistance of the resin due to the addition of functional groups to its structure. When measured on a wet basis, the capacity increases as cross-linkage increases. Fewer functional groups are introduced into the

resin therefore the resins are spaced closer together. Since the volume of water is reduced by the increased cross linkage, the capacity of the resin increases. The maximum resin capacity, also known as breakthrough capacity, is dependent on the pH, grain size, column size, and flow rate.

Equilibrium Rate

The time for a system to reach equilibrium is influenced by the cross-linkage of the resin. The higher the cross-linkage, the more resistant it is to the diffusion of ions therefore leading to increased time to equilibrium. Pore size also has an affect on the operating rate, for example, zeolite exchangers operate slower while an ion-exchanger containing larger pores operates faster [38]. The spherical particles of the ion-exchange resin resist the flowing of a liquid through or around them. The smaller the resin bead size, the greater the resistance will be against which the liquid must flow. Diffusivity is a controlling factor in the time that it takes for a particular system to reach equilibrium.

3.5 Applications in Industry

When designing an ion-exchange column, it is important to have an understanding of how the chemical separation process works. Chemical separation is broken down into two sections; the specific chemistry of the separation which includes the affinity that the resin has for the target molecules, and the engineering of the separation column which consists of the dimensions, flow rates, and other parameters specific to the process. It is recommended that an analysis be performed under equilibrium conditions. Determination of the equilibrium isotherms allow for comparison between the

various resins that are commercially available, and to explore optimal regeneration conditions. Any tests that can be performed using the exact process stream would be valuable in determining if the presence of any addition ions in the solution will compete for the exchange sites. In industrial applications, most ion-exchange processes take place in columns to take advantage of multiple equilibrium steps. Upon completion of the equilibrium isotherm evaluation a variety of resins can be chosen and tested to pinpoint which resin is the most efficient and also determine the operation parameters for scale-up. This allows for calculation of capital and operational costs of the separation media, and the life expectancy of the resin.

The interest in the ion-exchange process as a solution to wastewater disposal issues is due to its ability to remove trace impurities from the bulk of a substance. The use of ion-exchange for the recovery of valuable metals in solution is one of its major applications in industry. Metals, such as copper and zinc, are recovered from waste streams, often at a profit, solving waste disposal problems [22].

An example where ion-exchange has been used to treat dilute waste streams analogous to hydrometallurgical waste streams has been presented by Ewing, Evans and Doyle (2003) [49]. A study was presented where plating additives were used to recover copper from a dilute aqueous solution with the chelating resin DOWEX M4195. Ion-exchange was utilized in this study to remove copper from the waste stream in an industrial facility involved with the manufacturing of semi-conductors. The process stream was used in the manufacturing process and through the use of ion-exchange the stream was purified to the point where it could be re-used. This eliminated the need for outsourcing the waste control to exterior companies and it was proven to reduce the need for water which is scarce in the locations where semi-conductor manufacture is prevalent.

Mijangos and Diaz (1990) [14] present a simple method on how to fit equilibrium results for a multi-component system to an analytical equation. This can be useful in the design of process plants to recover the low concentration constituents in the waste stream. The use of ion-exchange to recover metals from the wastewater of a hydrometallurgical process is also presented. Ion-exchange was utilized to reduce contamination of the waste and to improve the profitability of the project by recovering more of the valuable metal from the waste solution. The implementation of ion-exchange presented various hurdles before it could be designated a viable solution. The first hurdle was that the effluent stream had a low concentration of constituents and is associated with high flow rates. Precipitation must also be avoided to allow the ion-exchange resin to remain porous and receptive to appropriate ions. The degree to which these issues affect the viability of the ion-exchange process depends on the specific components of the waste stream. The complex sulfide hydrometallurgical process reviewed in this study proposes a selection of potential commercial resin candidates. The selected resins were placed in the industrial solution for eight hours to ensure equilibrium was achieved. The pH of the solution was varied to highlight the sensitivity of the equilibrium reaction to pH.

During experimentation it was found that the concentrations of certain metals in the solution had to be altered to avoid precipitation. The industrial solution is identified in Table 3.3. Based on this solution a total of twelve commercial resins were identified. They are macroporous and of the polystyrene-divinylbenzene type and are listed in Table 3.4. In addition to the commercial resins, three chelating ligands were used. These ligands were chosen by the experimenters based on availability and their selectivity toward certain metals.

The distribution coefficient, K_D , is defined as the ratio of the concentration of the so-

lute in the stationary phase to that in the mobile phase under equilibrium conditions. It is a measure of the nature and strength of the intermolecular forces between the solute and the two phases. Solutes that interact more strongly with the stationary phase will exhibit a larger distribution coefficient and will be retained longer. Table 3.5 shows the distribution coefficients of the resin considered.

Table 3.3: Composition of sulfide hydrometallurgy waste-water effluent [14])

Component	Composition (mg/L)
Sodium	37000
Iron	14000
Potassium	3000
Zinc	800
Calcium	450
Manganese	400
Nickel	150
Copper	130
Cobalt	120
Cadmium	70
Lead	50
Sulfate	90300
Chloride	28000
Solid in Suspension	20
Average Solution pH	1.80
Density	1140 kg/m ³

The twelve resins chosen were categorized and some were eliminated based on their attributes. For example, the quaternary amines were eliminated from the study based on their low distribution coefficients indicating that the anion complexes will not form. The sulfonic and carboxylic type resins show low retention due to the interference of iron ions. The remainder of the study concentrated on iminodiacetic resins which were known to be more effective.

Results from the experimentation indicated that it was necessary to work in the acidic region of the pH scale to avoid precipitation of the basic species. Secondary exper-

	Group											
	Sulfonic				Carboxylic		Quater. Amine	Amidoxine	Iminodiacetic			Aminophos.
Resin	L S100	L SP112	D C20	D C26	L CMP80	D C464	L MP500	D ES346	L TP207	D ES466	A IRC718	D ES467
Bead size distribution (mm)	0.3-1.25	0.3-1.2	0.3-1.2	0.3-1.2	0.3-1.2	0.3-1.2	0.3-1.5	0.3-1.1	0.3-1.2	0.3-1.2	0.3-1.2	0.3-1.2
Ionic form	Na	Na	Na	Na	H	H	Cl	chelate free	Na	Na	Na	Na
Density (kg m ⁻³)	1280	1270	1250	1250	1180	1130	1060	1100	1170	1050	1140	1120
Total capacity (eq l ⁻¹)	2.2	1.8	2.0	1.85	4.8	3.5	1.2	—	2.7	—	1.0	—
Moisture content	42-45	40-45	43-50	47-52	45-50	57-62	55-60	55-60	45-50	55-60	69	60-65

Table 3.4: Commercial resin properties [14]

Table 3.5: Distribution coefficients (K_D) of commercial resins (shown in Table 3.4) [14]

Ligand	pH	Co	Ni	Cu	Zn	Mn
Iminodiacetic	3.4	15-55	130-200	1200	17-30	2
Aminophosphonic	3.9	22	< 1	79	30	5
Amidoxime	3.9	2	< 1	1200	4	< 1
Sulphonic	2.4	1	1	2.5	1	1
Carboxylic	1.7	3	< 1	1	2	2
Quater. Amine	1.5	2	< 1	6	57	< 1

imentation was necessary because theoretical equations of solubility did not predict the reality of complex solutions. These experiments were designed to determine the pH levels with a higher degree of accuracy. It was found that the pH should remain below 3.3 to avoid precipitation and clogging of the resin bed, as shown in Figure 3.12, where C is the concentration of the residue (precipitate) and C_o is the initial concentration.

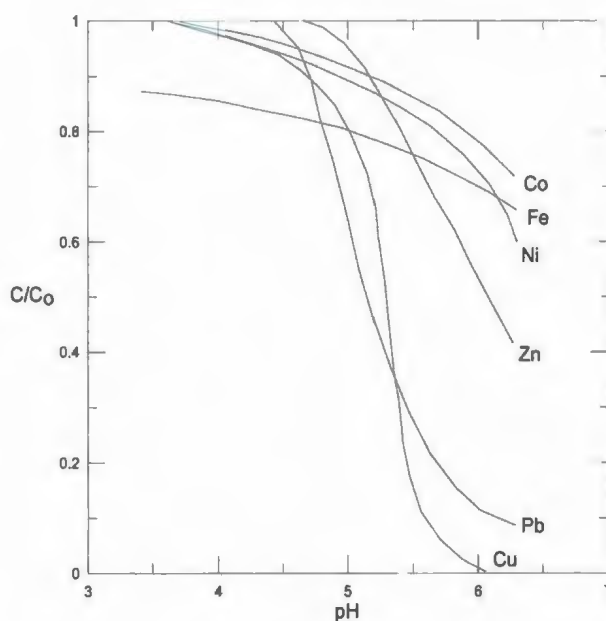


Figure 3.12: Residual Concentration of Metals as a Function of pH [14]

The experimental results also show the kinetics of the metals for the iminodiacetic resin in a stirred tank, shown in Figure 3.13. This figure shows that copper and nickel are retained more effectively than other ions and it takes a longer duration of time for other metals to reach equilibrium.

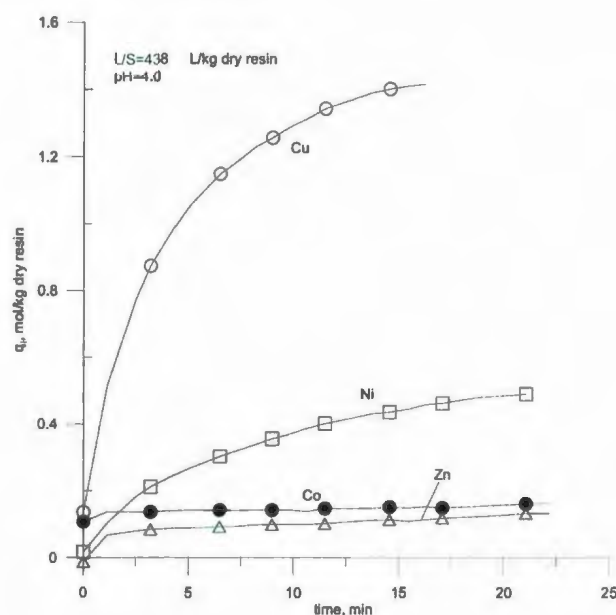


Figure 3.13: Kinetics of the Simulation Loading of Metals in a Stirred Tank [14]

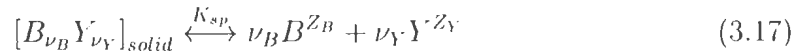
Further experiments were carried out by changing the solid/liquid ratio and the pH of the solution at equilibrium. From here, isotherm equations were determined based on the assumption that they are binary in nature (for a balance between accuracy and simplicity).

The conclusive results from the studied support the use of iminodiacetic resins to treat wastewaters from complex sulfide hydrometallurgy. The resin shows good selectivity and has the ability to recover valuable metals from waste streams. The proposed procedure presented in the study may be used to study other industrial waste streams and the applicability of other commercial resins. Due to the importance of modeling

the kinetics, and in fitting equilibrium data, these experiments give an important indication of process viability.

De Villiers, Van Deventer and Lorenzen [39] present a method to recover valuable metals from sparingly soluble solids in a slurry mixture from a percolation leaching procedure. Leaching is important in most hydrometallurgical extraction processes as it involves the freeing of metals from solid ores by chemical dissolution.

In the slurry mixture, a dissociation equilibrium exists between the dissolved ions in the solution and the solid ore. When the ions in the solutions are removed by some process (such as ion-exchange) the solid will continue to dissociate to regain equilibrium (and to satisfy Le Chatelier's principle). Complete liberalization of the desired ions from the solid ore is possible provided a sufficient amount of resin is available for the exchange. A general representation of the dissociation reaction (Le Chatelier's principle) is as follows:



where

$$K_{sp} = [a_B]^{\nu_B} [a_Y]^{\nu_Y} = [C_B \gamma_B]^{\nu_B} [C_Y \gamma_Y]^{\nu_Y} \quad (3.18)$$

where $B_{\nu_B} Y_{\nu_Y}$ represents the solid ore being dissolved, B^{Z_B} represents the constituent cation (valuable species), Y^{Z_Y} represents the anion (contaminant species), K_{sp} is the solubility product, C_i is the solubility phase concentration, a_i is the activity, γ_i is the activity coefficient, ν_i is the number of moles of constituent i, and z_i is the valence of the species.

During the leaching process the concentration of the constituent cation increases. According to the above equation this will cause an associated increase in contaminants as well. This means that more leaching agent is required to obtain an optimized amount of valuable metal recovered. For this reason a multi-stage leaching process is employed such that the contaminants removed from one stage will not affect the leaching in the next stage.

In order for the ion-exchange to be successful the stoichiometric equivalent of the cation of the mineral species must exist in the resin and migrate during the reaction to maintain electro-neutrality. When this cation is available in excess, the resin is referred to as a strong acid cation or a weak base anion-exchange resin. When the cation is part of the functional group it must be activated in order for the ion-exchange process to work. This is known as a weak acid cation or weak base anion-exchange resin. When the cation is part of the mineral species it is known as a chelating resin.

The solubility of the sparingly soluble solid is affected by the change in the chemical composition caused by the exchange of ions from the resin. It can be described mathematically:

$$S = \left(\frac{K_{sp}}{[\nu_B \gamma_B]^{\nu_B} [\nu_Y \gamma_Y]^{\nu_Y}} \right)^{\frac{1}{\nu_B + \nu_Y}} \quad (3.19)$$

The increase in concentration of the valuable species (B^{ZB}) and the contaminant (Y^{ZY}) shifts the equilibrium condition by increasing the concentration of the ion common to the equilibrium reaction. This is known as the common ion effect. This reduces the solubility of the mineral species as can be shown in the following equation.

$$K_{sp} = [\nu_B S \gamma_B]^{\nu_B} [(\nu_Y S + m) \gamma_Y]^{\nu_Y} \quad (3.20)$$

where m is:

$$m = \frac{|z_A| C_A}{|z_Y|} \quad (3.21)$$

To counteract this behavior it is suggested to try either of the following procedures:

- Use the proper counter-ion species to initially saturate the resin to transform the contaminant species so it does not take part in the dissolution reaction.
- Precipitate the contaminant ion when there is no electrolyte sorption. Existence of electrolyte sorption would cause precipitation within the pores of the resin.

The thermodynamic equilibrium constant can be written as:

$$K_A^B = \frac{(y_B \gamma_B)^{Z_A} (C_A \gamma_A)^{Z_B}}{(y_A \gamma_A)^{Z_B} (C_B \gamma_B)^{Z_A}} \quad (3.22)$$

where y_i is the resin mole fraction.

The concentration of the species is given by:

$$C_B = \frac{|Z_Y| C_Y - |Z_A| C_A}{|Z_B|} \quad (3.23)$$

$$C_Y = \nu_Y S \quad (3.24)$$

$$C_A = \frac{Q(1 - \epsilon) D P R V y_B}{|Z_A| V} \quad (3.25)$$

where V is the solution volume, $DPRV$ is the volume of the resin, Q is the resin capacity, ϵ - volumetric fraction of interstitial water in a volume of resin beads and y_B can be found from the thermodynamic equilibrium constant as a function of the concentration of the contaminant species.

The thermodynamic dissolution coefficients for different resin-in-pulp slurries containing either a cation-exchange resin or an anion-exchange resin are given in Table 3.14

Dissolution Reaction	Cation Exchange Reaction	K_{φ}	K_A^B	K_{AB}
$ z_B = z_Y $	$ z_B > z_A $, $ z_B / z_A =$ integer	$(a_B)(a_Y)$	$\frac{(\overline{a_B})(a_A)^{z_A}}{(\overline{a_A})^{z_A}(a_B)}$	$K_{\varphi} K_A^B$
$ z_B = z_Y $	$ z_B > z_A $, $ z_B / z_A \neq$ integer or $ z_A > z_B $, $ z_A / z_B \neq$ integer	$(a_B)(a_Y)$	$\frac{(\overline{a_B})^{z_A}(a_A)^{z_B}}{(\overline{a_A})^{z_B}(a_B)^{z_A}}$	$[K_{\varphi}]^{z_A} K_A^B$
$ z_B = z_Y $	$ z_A > z_B $, $ z_A / z_B =$ integer	$(a_B)(a_Y)$	$\frac{(\overline{a_B})^{z_A}(a_A)}{(\overline{a_A})(a_B)^{z_B}}$	$[K_{\varphi}]^{z_A} K_A^B$
$ z_B = z_Y $	$ z_B = z_A $	$(a_B)(a_Y)$	$\frac{(\overline{a_B})(a_A)}{(\overline{a_A})(a_B)}$	$K_{\varphi} K_A^B$
$ z_B \neq z_Y $	$ z_B = z_A $	$(a_B)^{z_Y}(a_Y)^{z_B}$	$\frac{(\overline{a_B})(a_A)}{(\overline{a_A})(a_B)}$	$K_{\varphi} [K_A^B]^{z_Y}$
$ z_B \neq z_Y $	$ z_B > z_A $, $ z_B / z_A =$ integer	$(a_B)^{z_Y}(a_Y)^{z_B}$	$\frac{(\overline{a_B})(a_A)^{z_A}}{(\overline{a_A})^{z_A}(a_B)}$	$K_{\varphi} [K_A^B]^{z_Y}$
$ z_B \neq z_Y $	$ z_B > z_A $, $ z_B / z_A \neq$ integer or $ z_A > z_B $, $ z_A / z_B \neq$ integer	$(a_B)^{z_Y}(a_Y)^{z_B}$	$\frac{(\overline{a_B})^{z_A}(a_A)^{z_B}}{(\overline{a_A})^{z_B}(a_B)^{z_A}}$	$[K_{\varphi}]^{z_A} [K_A^B]^{z_Y}$
$ z_B \neq z_Y $	$ z_A > z_B $, $ z_A / z_B =$ integer	$(a_B)^{z_Y}(a_Y)^{z_B}$	$\frac{(\overline{a_B})^{z_A}(a_A)}{(\overline{a_A})(a_B)^{z_B}}$	$[K_{\varphi}]^{z_A} [K_A^B]^{z_Y}$

Figure 3.14: Thermodynamic Dissolution Coefficients [39]

DeVilliers et al. conducted experiments considering a number of commercial resins in various ionic forms. Different combinations of cationic and anionic resins were used to study the effect of the electrolyte solutions on the solubility of lead sulfate and the equilibrium resin loadings. After preparation of the resins (involving bead selection and bed rinsing) the equilibrium experiments were conducted. Different resins were added to one liter PVC bottles along with lead sulfate. The solutions were constantly stirred and allowed to react for one month which was felt to be sufficient length of time to obtain equilibrium. The mixture was then separated into a filtrate solution and resin beads. The resin beads were rinsed, dried, crushed, weighed, ashed, dissolved and put into a crucible. Both filtrate solution and bead remains were analyzed with an atomic absorption spectrometer and an ion emission spectrometer. The filtrate was also analyzed with an ion chromatograph.

The equilibrium isotherms for Pb^{+2} for a specific resin (Duolite C26) with variable ionic forms are given in Figure 3.15. It shows that a high resin loading can be obtained for low solution concentrations. This is important for dilute waste streams. The shape of the H^+ , Na^+ , and K^+ results are typical behaviors for modern synthetic ion-exchange resins.

Ion-exchange was proven to be a feasible method to recover valuable mineral species from the sparingly soluble solids due to the availability of "selective high capacity ion-exchange resins" [39].

McGarvey and Siber (1985) [5] discuss the use of ion-exchange units in the electroplating industry. Similar to the hydrometallurgical industry, there is a need to controlling the amount of toxic wastes that enter the environment. The rinse waters in the electroplating industry are dilute in metal concentrations and therefore the

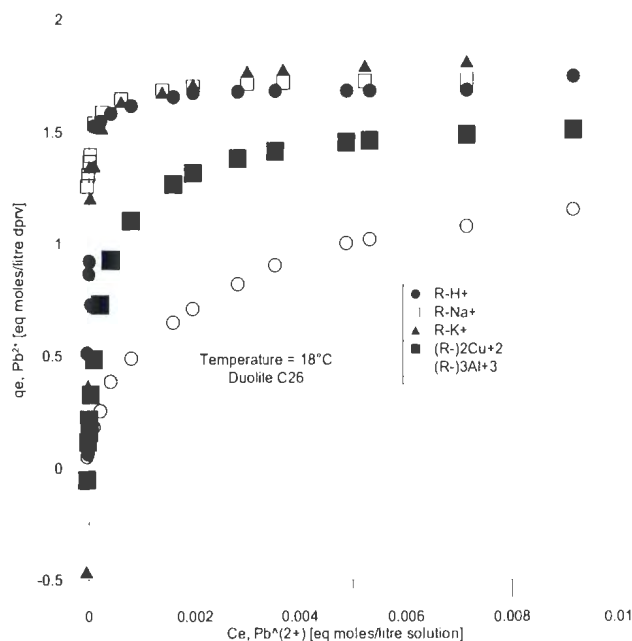


Figure 3.15: Equilibrium Isotherms for Sorption of Pb^{+2} ions for Duolite C26 Resin [39]

ion-exchange process could be successful with the use of ion-exchange resins acting as concentrators.

It is important to know all the components in the waste stream prior to applying ion-exchange technology. An example outlined by McGarvery and Siber [5] warns that the effectiveness of an ion-exchanger in a metal recovery plant failed to perform because the solution contained a substantial concentration (about 5%) of sodium chloride which was not considered in the initial design of the treatment plant. When there is the potential for the occurrence of highly dissociated salts such as sodium chloride, sulfuric acid, caustic, soda ash, etc. ion-exchange will frequently be eliminated as a possible separation technology due to the formation of various complexes that can pass through the resin unaffected. On the other hand, concentrated chloride solutions can be treated to remove iron and other metals which form chloride complexes.

Mijangos, Lombrana, et al. (1990) [26] studied the equilibrium and kinetic results for the recovery of products from a complex hydrometallurgical effluent using a chelating ion-exchange resin. A chelating resin containing iminodiacetic groups was chosen due to its capacity for the recovery of heavy-metals from hydromet effluents. The zinc industry produces a high flow of liquors with low concentrations of non-ferrous ions that have a high metallic value. Experiments were conducted on zinc raffinates where the separation of several species was considered such as sulphate, iron, copper and zinc. It was determined that the recovery of heavy-metals by ion-exchange resins play an important role in wastewater treatment.

Diaz et al (1998) [37] states that one benefit to the use of fluidized bed ion-exchangers over the conventional fixed bed system is the issue of clogging that takes place when dealing with dirty solutions containing suspended particles. Fluidized-bed ion-exchange operations have been developed especially for the treatment of solutions with suspended solids as is the case of hydrometallurgic industry wastewater. Fixed bed columns became clogged as the slurry passed through the column, and thus proved to be impractical in some cases. The fluidized bed system allows for better mass-transfer between the solid and the liquid phases due to the increased contact that takes place. The issues of concern with this system is the utilization of the regeneration solutions since in most cases, these solutions cannot be reused. This leads to some environmental and economic concerns.

Experiments were conducted by Diaz et al (1998) [37] in which testing a fluidized-bed ion-exchange system with a hydrometallurgical wastewater containing cobalt and copper as heavy-metal ions. The resin of choice was the chelating iminodiacetic type, Lewatit TP-207. Table 3.6 outlines the specific characteristics of the resin. This resin was chosen due to its different selectivity toward the two metallic ions (Co^{2+} and

Table 3.6: Characteristics of Lewatit TP-207 Resin [37]

Ionic form supplies	Na
Matrix	Polystyrene
Ionogenic groups	Iminodiacetic
Size (mm)	0.3-1.25
Apparent density (kg/m ³)	700-800
Humidity (% weight)	45-50
Color	Beige clear
Total capacity (mol/l in II form)	2.7
Thermal stability (° C)	-20 to 80
pH stability	1-14

Cu²⁺).

The wastewater that was introduced to the system was a mixture of cobalt (35 mg/L) and copper chlorides (33 mg/L) with 20 g/L of NaCl to adjust the salinity. The eluent solution was 3% HCl with 20 g/L of NaCl to maintain the same salinity as the loading column. The flow rate was 110 L/h in both columns.

The system operates in two modes; elution and division. At cyclic steady state, the equipment can split up the wastewater producing an effluent concentrated in cobalt in the outlet stream of the loading column (saturation) and a concentrated stream of copper in the effluent of the elution column (elution).

In the elution mode, shown in Figure 3.16, saturation takes place in one column, while elution with hydrochloric acid (HCl) occurs in the other column. This set up is similar to two fixed-bed operation columns where the function of each column is changing at the end of the operation cycle. The solutions (load and elution) enter the columns from the bottom and cross the interstage separators in the column. Load and regeneration occur at the same time, until the columns are both saturated and regenerated. Then the feed is cut off and the two valves under the columns are opened

causing the resin of each stage to fall one level below. The used resin is collected in a tank at the bottom under the column which then moves to the opposite column to undergo regeneration. Under ideal conditions, the effluent of the loading column is where cobalt is concentrated, and the effluent of the elution column is where copper is concentrated.

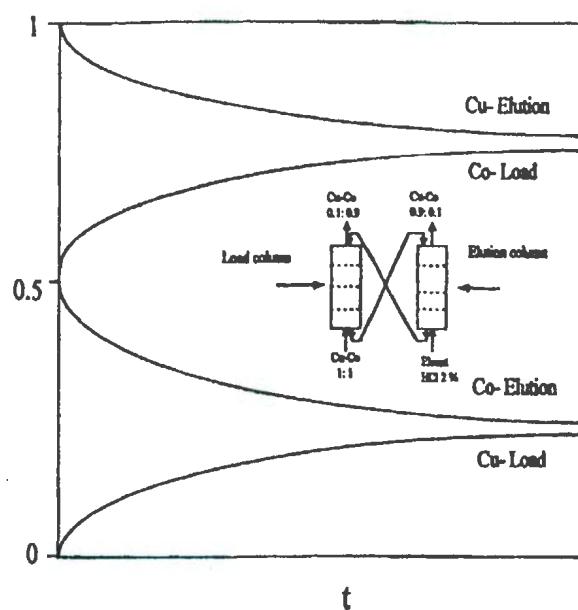


Figure 3.16: Elution Operation Mode for Column Type Ion Exchange [37]

The division operation mode, shown in Figure 3.17, the wastewater is introduced at various pH levels into each column. The effluent of the column at high pH is diluted with respect to the initial wastewater and it is more concentrated in the ion that is retained less by the resin. The effluent in the other column (at low pH) is more concentrated with respect to the initial wastewater, and more concentrated in the ion that is retained more by the resin. The operation involves falling and transfer of the resin which is the same as the elution mode.

The experiments were conducted using the elution operation mode to split-up a hy-

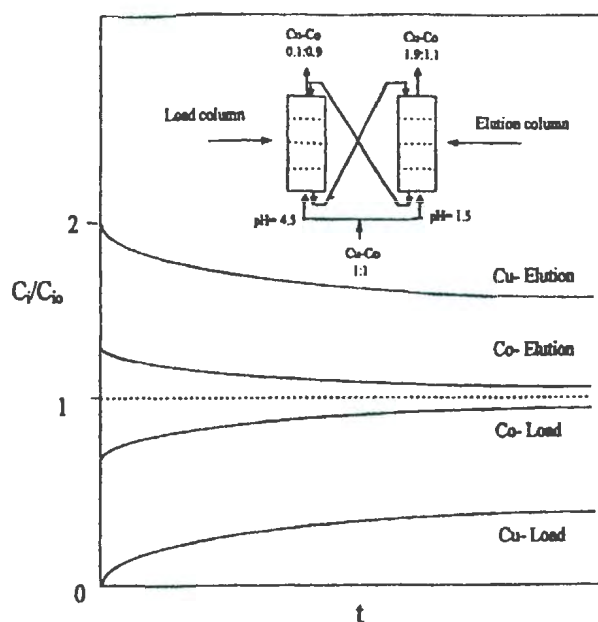


Figure 3.17: Division Operation Mode for Column Type Ion Exchange [37]

hydrometallurgical wastewater and it was found that cobalt went with the effluent of the loading column and copper with the effluent in the elution column. 90% of copper and cobalt initially in the mixture were recovered from the two streams. It was determined that this proposed system can be used for separation and concentration of streams that have components with different equilibrium isotherms depending on system pH or temperature or both.

3.5.1 Feasibility Considerations

To determine the feasibility of ion-exchange usage in hydrometallurgy, a sufficient number of tests should be conducted to determine important parameters influencing the efficiency at a commercial scale. Developing an ion-exchange process for waste treatment for field implementation has been discussed by Mijangos and Diaz (1989)

[14] and Mindler [22] and include the following steps:

1. Research the specifics of the waste stream. Identification of the most recent and efficient types of ion-exchangers and resins available is important at the early stages of plant design. A range of commercial resins can be chosen for further analysis.
2. Preliminary lab work. This stage includes determination of working conditions and pH levels where precipitation may occur. This is also where the selection of the resin may occur.
3. Laboratory tube work. The optimum design conditions for the resin are established and studied analytically to determine the reclamation procedure for the resin as well as its limitations and capacity. This may involve the development of equilibrium isotherms.
4. Pilot plant testing. When there is no history for treatment of the waste stream or design environment then testing at a larger scale may be helpful in identifying any possibility of chemical poisoning or other problems which may occur.
5. Commercial scale equipment design.

3.5.2 Process Limitations

Although ion-exchange processes have been widely accepted as a prominent method of recovering metal and purifying waste streams there are some inherent limitations. Such limitations have been noted in the literature [22].

Process limitations

- Interfering ions: can cause a portion of the capacity of the ion-exchanger to become exhausted before the desired expected retention levels have been reached.
- Separation: special processes are necessary to separate closely related ions.
- Further processing: recovered metal from ion-exchange generally needs further processes for commercial viability to be realized.

Physical Limitations

- Temperature: certain exchangers can only withstand certain temperatures for short durations which may limit the design or efficiency of the process.
- Physical poisons: blockages of the pores of the resin may reduce the capacity or rate of reaction of the process, or both.
- Turbidity: particles in the working solution can cause a high pressure drop or channeling of the solution through the bed such that reclamation of the resin may be less efficient.

Chemical Limitations

- Limiting Concentrations: there may be certain maximum concentrations of ions for economic feasibility.
- Chemical Poisons: certain ions, if not removed during regeneration and/or elution can build up and influence the rate of reaction.

3.6 Conclusions

The unavailability of specific details regarding the INCO waste stream makes it difficult to make specific conclusions about ion exchange techniques. This chapter discusses literature available on the technology and specific details that should be considered when modeling ion exchange in any processing facility on a general level. It is meant to provide a fundamental knowledge base for more detailed work. There are numerous types of ion exchanger techniques available. Further details on INCO's waste stream are required to determine potential application of any single ion exchange technology.

Chapter 4

Membranes

Membrane technology is becoming a popular separation and purification process. Advancements over the last 30 years have allowed membrane processes to become a feasible separation technology in a number of industrial applications. The increased number of synthetic materials identified as commercially viable membrane materials offer unique and novel solutions to specialized separation problems [52]. Continuous research and development has resulted in a better understanding of the fundamentals of membrane separation, improved transport properties, and enhanced thermal and chemical stability of the membrane body [53].

Membrane processes have been used in a variety of applications from the desalination of sea and brackish water to treating industrial effluents [53]. They are capital and energy efficient when compared to conventional separation processes and can be compact and modular [52].

Membranes allow for the combination and hybridization of separation technologies to improve process effectiveness leading to innovative solutions for specific applications.

4.1 Fundamentals

Mass transfer is the exchange or movement of a component in a mixture from one location to another due to a concentration gradient. This exchange occurs in the direction of high to low concentration (although other driving forces may exist). Mass transfer occurs by two mechanisms: molecular diffusion and eddy diffusion. The major difference between the mass diffusion types is the magnitude of movement of molecules and in the type of flow (laminar for molecular diffusion and turbulent for eddy diffusion). Molecular diffusion occurs on the molecular level where microscopic movement of individual molecules are considered. Eddy diffusion occurs in the bulk fluid motion where large groups of molecules are of interest. This chapter will concentrate on molecular diffusion as it is the most common type of mass transfer in commercial separators [36].

4.1.1 Mass Transfer Laws

Molecular mass transfer is governed by Fick's law which is analogous to Fourier's first law of heat conduction. For a mixture with two components A and B, the following equations represent the relationship between molar flux and concentration gradient.

$$J_{A_z} = -D_{AB} \frac{dc_A}{dz} \quad (4.1)$$

$$J_{B_z} = -D_{BA} \frac{dc_B}{dz} \quad (4.2)$$

where J_{i_z} is the molar flux, D_{AB} and D_{BA} are the diffusion coefficients between

components A and B, and $\frac{dc_i}{dz}$ is the concentration gradient in the z-direction (which is negative to the direction of ordinary molecular diffusion) [36].

Another mathematical model that can be used to represent mass transport phenomena is based on an equation that connects the fluxes of the electrical charges, volume (viscous flow), and individual components with the driving forces by a linear relationship [53]:

$$J_i = \sum_k L_{ik} X_k \quad (4.3)$$

where J_i is the molar flux, X is a generalized driving force, subscripts i and k refer to individual components, volumes, and electrical charges, and L is a phenomenological coefficient relating the fluxes to the driving forces. This equation is applicable to any membrane since it is independent of the membrane structure.

For multi-component systems Equation 4.3 can be written as a matrix in which the diagonal coefficients relate the fluxes directly to the corresponding driving forces, and the cross-coefficients express the coupling of fluxes with non conjugated driving forces [53].

Maxwell and Stefan have developed an expression for membrane based processes in which the forces are expressed as a linear function of the fluxes:

$$X_i = \sum_k C_i f_{ik} (v_i - v_k) = \sum_k C_i \frac{R_g T}{D_{ik} (v_i - v_k)} \quad (4.4)$$

where X is the driving force, D is the diffusion coefficient, R_g is the gas constant, C is the concentration, v is the linear velocity, and f is the friction coefficient.

Equation 4.3 and 4.4 are used to provide a complete description of transport processes through a membrane separating two homogeneous mixtures. It is limited in its application in a heterogeneous medium with viscous flow [53].

4.1.2 Mass Transfer Velocities

The velocities of the molecules in mass transfer is also a useful parameter to formulate. The velocities can be calculated first by looking at the molar average velocity of the mixture (v_M);

$$v_M = \frac{N_A + N_B}{c} \quad (4.5)$$

where N_i is the molar flux, v_A and v_B are component velocities, and c is the total concentration.

Using the concentration fraction, $x_i = c_i/c$, the following equation can be found for the mixture velocity:

$$v_M = x_A v_A + x_B v_B \quad (4.6)$$

Using the diffusion velocity ($v_{iD} = J_i/c_i$), mixture velocity ($v_i = v_M + v_{iD}$), and equation 4.5 the molar flow rate per unit area can be found to be:

$$N_A = \frac{n_A}{A} = x_A N + c D_{AB} \frac{dx_A}{dz} \quad (4.7)$$

and

$$N_B = \frac{n_B}{A} = x_B N + c D_{BA} \frac{dx_B}{dz} \quad (4.8)$$

where n_i is the molar flow rate and A is the mass transfer area. The first term on the right represents the bulk flow and the second term represents the ordinary molecular diffusion. The two limiting cases which bound the relationships are equimolar counter diffusion (EMD) and unimolecular diffusion (UMD). In equimolar diffusion the fluxes of A and B are the same in magnitude but opposite in direction. This situation is approached during distillation procedures. Unimolecular diffusion is when one component is transferred through a stagnant component.

4.1.3 Diffusion Coefficients

Many correlations exist to estimate diffusion coefficients. Diffusion coefficients for liquid mixtures are not easily estimated because there is no rigorous model that adequately represents the liquid state however some of the more popular approaches are mentioned here.

Diffusion Coefficients in Liquids

The Stokes-Einstein equation assumes that a dilute solute (A) has large, rigid, spherical molecules transferring through a solvent that is stationary (B) with small molecules and with no slip. This equation is limited in terms of its application however it acts as a solid base for other correlations.

$$(D_{AB})_{\infty} = \frac{RT}{6\pi\mu_B R_A} \quad (4.9)$$

where R_A is the radius of the solute molecule, μ_B is the solvent viscosity, and T is the temperature.

An extension of this equation is the Wilke-Chan equation:

$$D_{AB} = \frac{7.4 \times 10^{-8} (\phi_B M_B)^{\frac{1}{2}} T}{\mu_B v_a^{0.6}} \quad (4.10)$$

where ϕ_B is the association factor for the solvent which is 2.6 for water, v_a is the liquid molar volume of the solute at its normal boiling point, and M_B is the molecular weight. This equation gives good prediction where the solute molecules are small and the solvent is water.

When dealing with other solvents it is appropriate to use or derive different correlations to represent diffusion coefficients. For example, a correlation developed by Hayduk and Minhas shows good agreement where methanol, ethanol and unassociated solvents are used. This equation is split into two parts, the dilute representation of one normal paraffin to another and the nonaqueous solution.

Dilute Solution:

$$(D_{AB})_{\infty} = 13.3 \times 10^{-8} \frac{T^{1.47} \mu_B^{\epsilon}}{v_A^{0.71}} \quad (4.11)$$

where

$$\epsilon = \frac{10.2}{v_A} - 0.791 \quad (4.12)$$

General Nonaqueous Solution:

$$(D_{AB})_{\infty} = 1.55 \times 10^{-8} \frac{T^{1.29} (\mathcal{P}_B^{0.5} / \mathcal{P}_A^{0.42})}{\mu_B^{0.92} / \nu_B^{0.23}} \quad (1.13)$$

where \mathcal{P} is the parachor defined as $\mathcal{P} = \nu \sigma^{1/4}$ and σ is the surface tension. The preceding equations have limitations such as the solvent viscosity should not exceed 30 cp.

Limitations for any correlation used to predict diffusion parameters should be understood before undertaking a complete analysis [36].

Diffusion Coefficients in Solids

There are many parameters which must be considered when addressing diffusivity in solids. The diffusing atom affects the diffusivity and can be either a molecule or an ion. Another parameter is the nature of the solid structure. This includes whether the structure is porous or nonporous, crystalline, or amorphous. Whether the structure is metallic, ceramic, polymeric, biological, or cellular also affects diffusivity. A number of these parameters can be further classified into the types of bonding they may have in terms of covalent, or ionic bonding, or both. Even with all of these complexities, if a diffusion coefficient exists which properly captures the mass transport of the problem then Fick's law can be applied to the situation.

It is beneficial to mention diffusion in porous solids because the methodology can be applied to membrane separation. There are three mass transfer mechanisms that may take place either individually or in combination with one another.

1. Ordinary molecular diffusion through pores.
2. Surface diffusion based on concentration gradients.

3. Bulk flow through the pores.

When it is adequate to consider that diffusion only occurs in the pores then an effective diffusivity is commonly used. This is based on the total cross-sectional area of the solid (not the pore) and on a straight path (instead of the pore path). If pore diffusion can be described in terms of the ordinary diffusion coefficient D , then the effective diffusion coefficient can be written as:

$$D_{eff} = \frac{D\epsilon_K}{\tau} \quad (4.14)$$

where ϵ_K is the fractional porosity and τ is the pore path tortuosity which is the ratio between the pore length and the length of the pore if it were straight in the direction of diffusion. These parameters can be determined experimentally [36].

There are other solids which can be considered when studying diffusion, such as crystalline, metals, silica, glass, ceramics and polymers however they are outside the scope of this research.

4.2 Membrane Separation Process

A membrane separation process involves a mixture of two or more components, known as the feed, which is partially separated by a membrane (a semi-permeable barrier that allows select components to pass through it faster than others). The membrane separates the feed stream into two streams: the permeate, which is the stream that travels through the membrane, and the retentate, which is the stream that does not go through the membrane. In some cases, an additional wash or strip stream may be

needed on the permeate side to ensure continuous movement of the feed mixture. A simplified membrane system is shown in Figure 4.1.

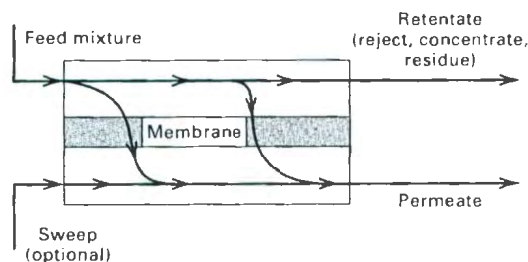


Figure 4.1: General Membrane System [36]

The membrane acts as an interface between two bulk phases providing a large surface area to volume ratio for separation. In order for separation to take place, one species in the mixture must be exchanged in preference for others. One bulk phase is enriched while the other is depleted of the component of interest.

4.2.1 Driving Forces

Transport takes place through a membrane by one or more driving forces such as convection or diffusion of individual molecules; induced by an electric field causing a migration of ions; or by a concentration, pressure, or temperature gradient leading to convection of mass [53, 54].

The performance of a membrane in a separation process is determined by the transport properties for different components in a mixture. Transport rate is determined by the permeability of the component in the membrane and by the driving force. Some of the driving forces include: pressure-driven processes (reverse osmosis, ultrafiltration, and microfiltration); partial-pressure-driven (prevaporation); concentration-gradient-driven (dialysis); and electrical-potential-driven (electrolysis and electrodialysis) [52].

In order for a membrane to be effective in separating a mixture of chemical components it must have both a high permeance as well as a high permeance ratio for the two species being separated. Permeance for a given species diffusing through a membrane of a given thickness is analogous to a mass transfer coefficient.

The molar transmembrane flux (N) of a species i is:

$$N_i = \left(\frac{P_{M_i}}{l_M} \right) (\Delta p_i \text{ or } \Delta c_i) = \bar{P}_{M_i} (\text{driving force}) \quad (4.15)$$

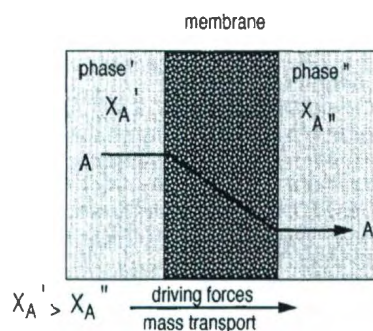
where P_{M_i} is the permeance, which is defined as the ratio of P_M (the permeability), to l_M (the effective membrane thickness). The driving force is described by the use of a partial pressure difference (Δp_i) or a concentration difference (Δc_i) across the membrane for species i .

The membrane selectivity between two species is defined as the separation factor α_{ij} for two species i and j :

$$\alpha_{ij} = \frac{C_i''/C_j''}{C_i'/C_j'} \quad (4.16)$$

where the prime and double prime represents upstream bulk phase flow (feed or retentate) and the downstream bulk phase flow (permeate). In some cases the pressure and concentration differences across the membrane are negligible, in which case, the separation factor is equal to the ratio of the permeabilities of the two species [52].

Figure 4.2 shows the transport of a component through a membrane from phase (') to phase (") due to a driving-force gradient. The driving force and transport mode for the membrane types are also shown [53]. Hydrostatic pressure (p), chemical potential



process	driving force	transport mode
microfiltration	Δp	convection
ultrafiltration	Δp	convection
reverse osmosis	$\Delta p (\Delta \mu_i)$	diffusion
dialysis	$\Delta C (\Delta a)$	diffusion
gas separation	$\Delta p (\Delta f_i)$	diffusion
pervaporation	$\Delta p_i (\Delta f_i)$	diffusion
electrodialysis	$\Delta \Phi$	migration

Figure 4.2: Mass Transport Modes [53]

(μ_i) , concentration (C), activity (a), partial pressure (p_i), fugacity (f_i), and electrical potential (ϕ_e) are the driving forces that take place in various membrane separation processes.

In some situations it is necessary to use a selective carrier in the membrane. The carrier can have mobility in the membrane or it can be fixed to the membrane structure. Figure 4.3 shows an example of facilitated transport in a liquid membrane. The transport of certain components can be co-current or countercurrent [53].

Liquid Permeation Membranes

In order for transport to occur in a liquid permeation membrane between two liquid phases divided by a liquid permeation membrane the solute molecules must be dif-

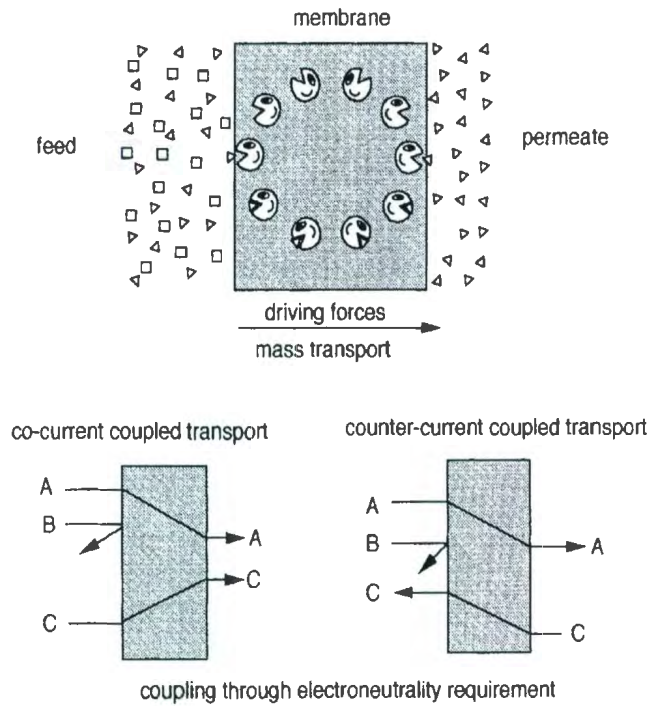


Figure 4.3: Facilitated Transport (Co-current and Countercurrent Transport) [53]

fused from the first liquid, through the membrane, and into the second liquid. The equilibrium distribution coefficient (K') is defined as:

$$K' = \frac{c_S}{c_L} \quad (4.17)$$

where c_S and c_L are the concentration of the solid membrane and the liquid, respectively. The flux equations through each phase are equivalent under steady state conditions and are defined in the following manner:

$$N_A = k_{c1} (c_1 - c_{1i}) = \frac{D_{AB}}{l_M} (c_{1iS} - c_{2iS}) = k_{c2} (c_{2i} - c_2) \quad (4.18)$$

where the subscripts 1 and 2 refer to the sides of the membrane (1 is side with a high concentration of molecule A), i is at the interface, and k is the associated mass transfer coefficient.

Acknowledging that $c_{1iS} = K'c_{1i}$ and $c_{2iS} = K'c_{2i}$ the following equation can be derived:

$$N_A = k_{c1} (c_1 - c_{1i}) = \frac{D_{AB}K'}{l_M} (c_{1i} - c_{2i}) - p_M (c_{1i} - c_{2i}) = k_{c2} (c_{2i} - c_2) \quad (4.19)$$

where p_M is the permeance of the solid membrane, l_M is the thickness, and D_{AB} is the diffusivity.

Solving these equations for the concentration difference and adding them together eliminates the concentrations at the interfaces and yields the following convenient equation for flux through the membrane:

$$N_A = \frac{c_1 - c_2}{1/k_{c1} + 1/p_M + 1/k_{c2}} \quad (4.20)$$

4.2.2 Membrane Characteristics

In order to choose which membrane process is appropriate for a desired separation, it is necessary to have an understanding of the principal characteristics of commercialized membrane separation technologies. The characteristics of membrane technologies used in industry are outlined in Table 4.1 and Table 4.2 which include the following parameters [52]:

- 1) Separation goal
- 2) Nature of the species retained (size of the species)

- 3) Nature of the species transported through membrane (electrolytic or volatile)
- 4) Minor or major species of feed solution transported through membrane
- 5) Driving force
- 6) Mechanism for transport and selectivity
- 7) Phase of feed and permeate streams

4.2.3 Membrane Material

Most industrial membranes are made from natural or synthetic polymers (macromolecules). Some examples of natural polymers include wool, rubber and cellulose. Synthetic polymers are produced by polymerization of a monomer by condensation (step reaction), or addition (chain reaction), or by the copolymerization of two different monomers [36]. Membranes can be homogeneous or heterogeneous, symmetric or asymmetric in structure, carry positive or negative charge, be neutral or bipolar, and be any one or a combination of the following: nonporous solid, microporous or macroporous solid with a fluid (liquid or solid) in the pores, a liquid phase with or without a second phase, a gel, or even a gas [36, 52].

Membranes often have a thin layer, called a skin, supported on a highly porous substructure. The separation characteristics in the thin layer are determined by the membrane material, pore size and the skin thickness. The porous sub-layer is a support for the thin and fragile skin layer, and does not aid in the separation process. The skin can be homogeneous or porous. Figure 4.4 shows the typical membrane materials and structure of various synthetic membranes.

Membrane performance is measured by high selectivity and fluxes; mechanical, chem-

Table 4.1: Characteristics of membrane separation processes [52]

TABLE 1-1. Principal Characteristics of Commercialized Membrane Separation Processes.

Separation Process	Separation Goal	Nature of Species Retained (Size)	Nature of Species Transported through Membrane	Minor/Major Species Transported	Driving Force	Mechanism for Transport/Selectivity	Phase of Feed and Permeate Streams
Gas permeation	Stream/streams enriched or depleted in a particular species	Larger species retained unless highly soluble	Gaseous. Smaller species/more soluble species	Either	Concentration gradient (partial pressure difference)	Solution-diffusion	Gaseous
Pervaporation	Same as above	Same as above	More soluble/smaller/more volatile nonelectrolytes	Preferably minor species	Concentration gradient, temperature gradient	Solution-diffusion	Liquid feed, gaseous permeate
Dialysis	Macrosolute solution free of microsolutes, microsolutes solution free of macrosolute	$>0.02 \mu\text{m}$ retained, $>0.005 \mu\text{m}$ retained in hemodialysis	Microsolute, smaller solute	Minor species. Solvent transported under osmotic unbalance	Concentration gradient	Sieving, hindered diffusion in microporous membranes	Liquid
Electrodialysis	Solution free of microions, concentrated solution of microions, fractionation of microions	Co-ions, macroions ^a and water retained	Microionic species	Minor ionic species, small amounts of water by electroosmosis	Electrical potential gradient, electro-osmosis (minor amount)	Counter-ion transport via ion exchange membranes	Liquid

Table 4.2: Characteristics of membrane separation processes (continued) [52]

Reverse osmosis	Solvent free of all solutes, concentrated solution of microsolutes	1- to 10-Å micro-solute species	Solvent. Species retained may be electrolytic or volatile	Major species solvent	Hydrostatic pressure gradient vs. osmotic pressure gradient	Preferential sorption/capillary flow (solution-diffusion-imperfection)	Liquid
Ultrafiltration	Solution free of macrosolute, macrosolute solution free of micro-solute, macrosolute fractionation	10- to 200-Å macrosolute species	Solution of micro-solutes	Major solvent, minor microsolutes	Hydrostatic pressure gradient vs. small osmotic pressure gradient	Sieving	Liquid
Microfiltration	Solution free of particles, gas free of particles	0.02- to 10- μ m particles	Solution/gas free of particles	Major solvent, minor microsolutes/ macrosolutes	Hydrostatic pressure gradient	Sieving	Liquid or gas
Emulsion liquid membrane	Stream/streams enriched or depleted in a particular species	Generally not size-selective except in host-guest chemistry	Species with high solubility in liquid membranes	Minor species. Can be major species in organic mixture separation	Concentration gradient, pH gradient	Solution-diffusion, facilitated transport	Generally liquid feed, emulsion containing permeate

*Macromolecules with charge.

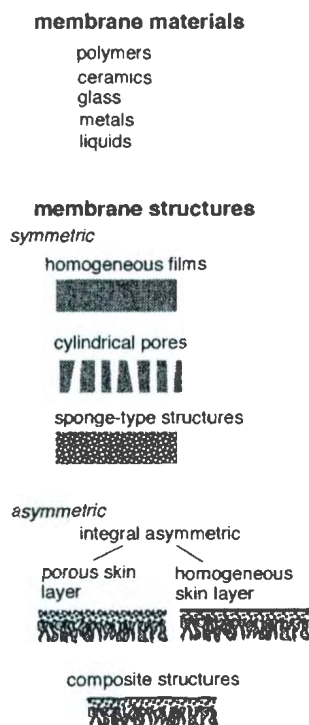


Figure 4.4: Materials and structures of membranes [53]

ical, and thermal stability under operating conditions; low fouling tendency; compatibility with the operational environment; cost-effective; and defect-free production [53]. The operational requirement of a membrane is that it must not dissolve, break-down, or disintegrate.

4.2.4 Membrane Shapes and Modules

Membranes can be cast as flat sheets, tubes, and fine hollow fibers. Figure 4.5 displays the common membrane shapes that are currently found in industrial applications: (a) flat asymmetric or thin-composite sheet; (b) tubular; (c) hollow fiber; and (d) monolithic.

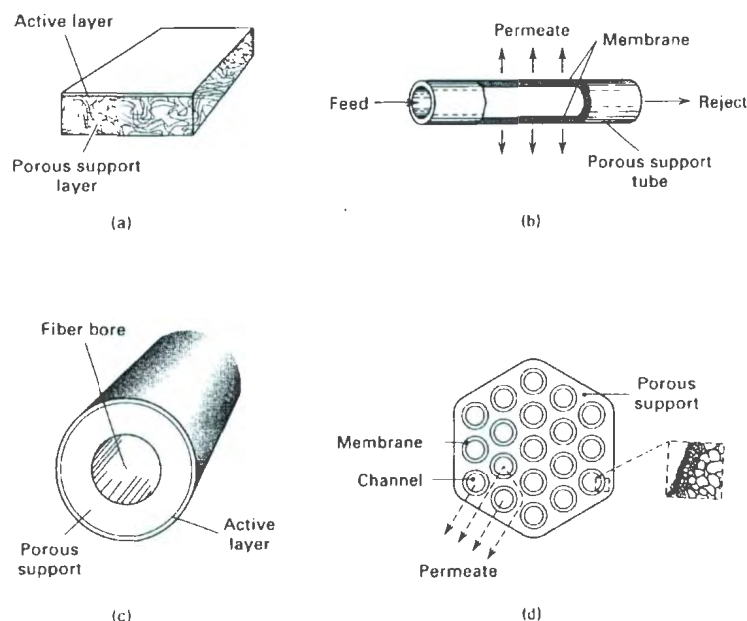


Figure 4.5: Membrane Shapes [36]

Membranes are installed in devices known as membrane modules. Figure 4.6 shows examples of membrane modules including (a) plate and frame; (b) spiral wound; (c) four leaf spiral wound; (d) hollow fiber; (e) tubular; and (f) monolithic. In some special applications, rotating cylinders and the transversal flow capillary module may be necessary [36].

Axial flow is the most commonly used flow type in capillary modules. Despite problems with flow distribution and mass transfer, this type of module is used due to its attractively low production costs and high packing density. These modules have straight membrane capillaries through the fiber lumen and the shell. On the other hand, a transversal flow capillary module utilizes perpendicular flow to promote turbulence at the membrane surface allowing for better control of concentration polarization effects compared to parallel flow. Another type of membrane module is the spiral-type tubular membrane which involves flow in a curved tube at high velocities

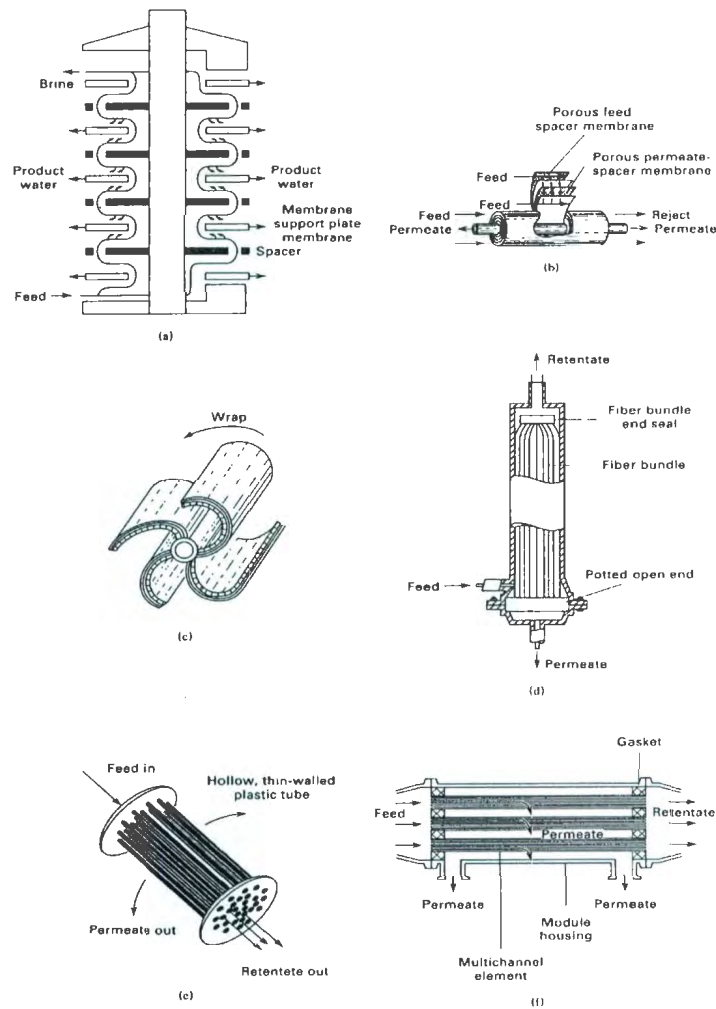


Figure 4.6: Membrane Modules [36]

causing centrifugal instabilities and increased flow from the membrane to the center of the tube. This concept is known as Dean flow or Dean vortices and can lead to an increase in flux for processes such as micro and ultrafiltration. Due to the high cost of implementing this technology, commercial scale applications have been limited [53].

4.3 Membrane Types

Membrane processes applicable to this study can be grouped into the following categories:

1. Liquid membrane - The membrane is surrounded by liquid phases on both sides. The concentration difference between the liquids drives the diffusion of the molecules.
2. Electrodialysis - Occurs by imposing an electromagnetic field across the membrane
3. Reverse osmosis - A membrane which reduces the flux of low molecular weight solute is placed between a solution and a pure solvent. The solvent diffuses into the solution by osmosis. When a reverse pressure gradient is imposed the flow of the solvent reverses.
4. Ultrafiltration - A pressure gradient is used to separate molecules on the basis of molecular weight by means of a semipermeable polymeric membrane.
5. Microfiltration - Similar to ultrafiltration however the molecule size is generally larger.

Liquid Membranes

Liquid membranes (LM) are capable of selective separation and concentrating pollutants from dilute aqueous solutions resulting in high treatment efficiencies [56]. Through the use of the LM process it is possible to simultaneously perform extraction and stripping in one stage, and thus achieve mass transfer characteristics that are

not limited by the condition of equilibrium. LMs have the potential of removing toxic substances from wastewater down to very low levels. Also, LMs are capable of reducing the levels of heavy-metal ions such as Cr^{6+} , Hg^{2+} , Cd^{2+} from several hundred ppm to 1 ppm [69].

Of the LM processes, the emulsion liquid membrane (ELM) and the supported liquid membranes (SLM) have been extensively studied and used in large scale applications. The development of the ELM as a selective removal technique has large potential in dilute wastewater treatment.

Emulsion Liquid Membranes

The use of ELMs was first commercialized in 1986 by two researchers simultaneously in Austria and China. Both applications involved the removal of contaminants from wastewater (zinc and phenol, respectively). Since that time, liquid emulsion membranes have become useful in a number of different industries [52].

ELMs are unique from other membranes in that they involve an emulsion configuration (example: water/oil/water or oil/water/oil). ELMs are also referred to as surfactant liquid membranes, liquid surfactant membranes, or liquid emulsion membranes. This type of membrane is generally prepared by forming an emulsion with two immiscible phases and then introducing a third continuous phase by agitation. During agitation, globules of emulsion form, providing a large surface area for mass transport. The membrane is the phase which houses the internal droplets of the emulsion and separates it from the continuous phase. The internal droplets and the continuous phase are normally miscible, however, the membrane must not be miscible in either phase if stability is desired [52]. A schematic of the emulsion liquid membrane is shown in Figure 4.7.

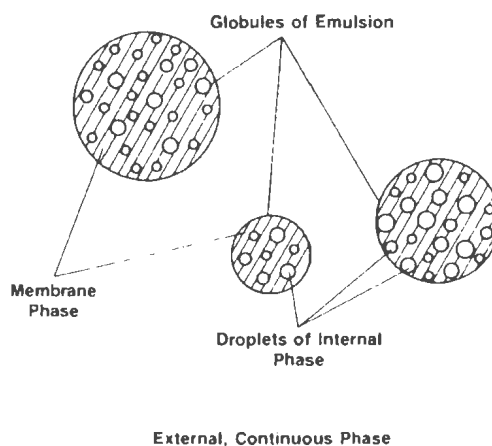


Figure 4.7: Emulsion Liquid Membrane System [52]

The transport of mass from one phase to the other may be enhanced through the use of additives and surfactants. These substances can provide selectivity and permeability through the membrane. Once separation is achieved in the emulsion, the phases are separated by gravity. The extracted component can be separated from the “loaded” phase by breaking the emulsion using an electrostatic coalescer [52].

Figure 4.8 shows a schematic of a continuous ELM process. This process takes place in four steps:

- (1) emulsification - formation of globules
- (2) dispersion of the emulsion in contact with the external, continuous phase for extraction
- (3) settling to separate the emulsion from the external phase
- (4) breaking the emulsion to recover desired product and the membrane phase for recycle

There are two types of driving forces involved with ELM. One type involves the

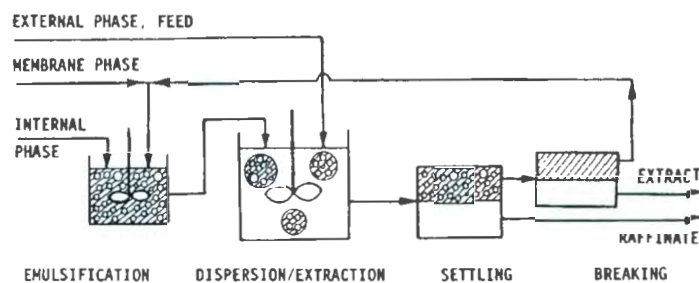


Figure 4.8: Continuous Liquid Membrane Process [52]

minimization of the diffusion species in the receiving stage creating a concentration gradient leading to a high extraction rate. The second type occurs when the diffusing species is carried across the membrane phase by using a carrier compound. In this type of driving force the reactions take place at the internal and external interface. The high extraction rate is facilitated through the continuous transport from the internal to external phase [52]. Both types allow for extraction and stripping to take place simultaneously.

ELMs have been applied to waters containing organic and inorganic pollutants. This process is applicable for heavy-metal separation from aqueous solutions, as well as liquids containing contaminants such as ferrous and non-ferrous metals, alkaline metals, radioactive elements and rare metals. Ho and Sirkar (1992) [52] list examples of processes where ELMs have been used for heavy-metal recovery zinc, cadmium, copper, and lead, from wastewater in metallurgical plants.

Advantages of ELMs include simple equipment and installation procedures; high transfer rates; low requirements of solvent/carrier reagent; single stage extraction and stripping; and the potential for the removal of metal ions from wastewater [56, 57]. Liquid membranes also provide the advantage of separating impurities and recovering

water simultaneously [64].

The difficulties in using this method arise in the determination of reagent that will allow selective extraction of specific pollutants to a desired level within a given time frame. ELMs occasionally experience emulsion swelling, membrane rupture, and is complicated in its operation which includes emulsion formation and breaking steps. Membrane rupture may takes place due to interfacial shear between continuous and membrane phases. There is also an issue with demulsification involving the coalescence of dispersed droplets into larger droplets with subsequent phase separation by gravity. In some cases it is possible to use electric field to avoid this problem, but this causes the use of ELMs to become energy intensive [56].

There are a number of issues that affect the rate of extraction and permeability through an emulsion liquid membrane. Membrane thickness has a direct influence on the permeability in that as the membrane thickness increases the permeability decreases. An increase in temperature leads to an increase in the extraction rate of the species of interest. During the initial stages of mixing, increasing the mixing rate leads to an increase in extraction rate. This can be explained by the increase in mass transfer coefficient, however, as mixing time increases the extraction rate drops due to the hydrodynamic instability of the membrane at higher speeds. The pH is an important issue in extraction rate and permeability, especially for carrier mediated transport. High values of the feed phase solute concentration will decrease the rate of separation, therefore making the ELM process effective for dilute waste streams where the feed concentration is lower. High treat ratio (volume ratio of emulsion to external phase) causes the extraction rate to increase due to the increased capacity of the membrane and the internal phase leading to enhanced permeation and stripping of the solute. Large amounts of stripping reagent concentration and volume fraction

of the internal phase has a direct effect on the possibility of emulsion swelling due to high osmotic pressure gradients that are created between the internal and external phases.

Experiments using emulsion liquid membrane separation technology on pollutants from wastewaters were aimed to identify factors that influence the mass transfer of chemical species from the feed phase to the receiving and concentrating phase. The liquid membrane approach for the treatment of wastewater was simple, rapid and efficient. Overall, it was discovered that choosing adequate and efficient reagents, hydrodynamic regime, time intervals and energy ranges of ELM resulted in increased treatment efficiencies [56].

Abou-Nemei and Peteghem (1992) [58] performed a study relating the effect of adding tri-n-butyl phosphate (TBP) to di-2-ethylhexyl phosphoric acid (D2EHPA) on extraction efficiency using an ELM process. The use of ELMs for metal ion extraction is applicable to both dilute and concentrated solutions. Unfortunately, most industrial effluents, natural mining waters or leaching solutions are composed of more than one metallic component and this can cause interference in the process of extraction of any one metal (known as the masking effect). The rate of metal extraction in the presence of other metals may also lead to a higher rate of extraction due to the catalyzing effect of impurities (the salting-out effect). The presence of various ligands in the feed, such as succinate, formate, salicylate or acetate, will catalyze the interfacial reaction of metal extractions in ELMs. Also the salt anions, such as sulphates, nitrates and chlorides, have been shown to have a certain impact on the kinetics of metal extraction.

Tests were performed on both a model solution and an industrial feed containing

a mixture of metallic species including sodium (Na^+), magnesium (Mn^{2+}), cobalt (Co^{2+}) in large concentrations and nickel (Ni^{2+}), iron (Fe^{3+}), and Chromium (Cr^{3+}) in trace amounts. The goal of performing tests on the model solution was to explain the effect of impurities and other components along with the metallic species in the industrial feed. It was determined that there is an optimal composition of the extracting mixture that was required to achieve a maximum extraction efficiency, 5.5 vol.% D2EHPA + 0.5 vol.% TBP. It was also found that the selectivity can be improved by altering the TBP concentration in the membrane phase [58].

Dalea et al. [64] took an analytical approach to considering the relationship between the amount of reagent, time and the hydrodynamic regime to study liquid emulsions.

Boyadzhiev and Kyuchoukov (1980) [63] have conducted a number of studies that show the advantages to the one-step extraction and stripping process, as a solution to the treatment of wastewater in industrial applications. The study shows that the efficiency of the extraction and pertraction process depends on the size of the contact area, the mass transfer coefficients involved, and the concentration gradient creating the driving force. It is stated that the most promising application of emulsion techniques is in wastewater treatment, including metal ion removal from dilute aqueous solutions.

From the experiments conducted, Figure 4.9 was developed where the kinetic curves show the aqueous phase concentration of zinc, lead, cadmium, and copper versus time.

The extraction process was feasible over a pH range of 5-7. The extraction efficiency reaches a maximum where the destruction of emulsions caused by the agitation of the system occurs. Optimum time required for maximum efficiency (approximately 3.5

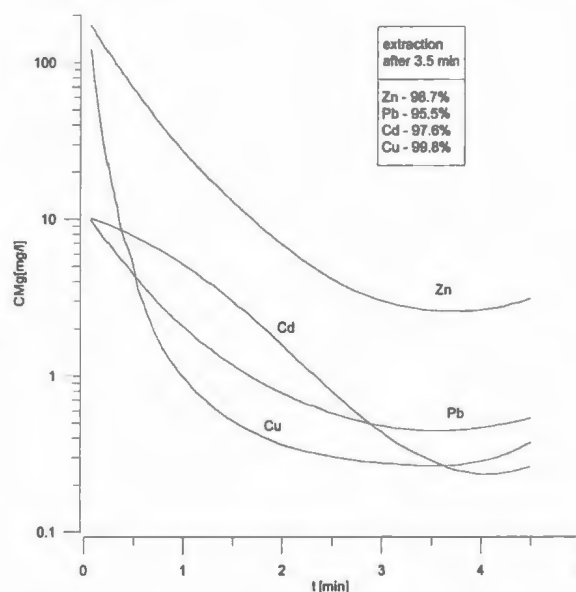


Figure 4.9: Kinetic curves for the removal of zinc, lead, cadmium, and copper ions in ELMs [63]

minutes) was found experimentally since it is dependent on a number of properties and hydrodynamic parameters. It was determined that the large interfacial area leads to high mass transfer rates even at low concentration gradients. This process can be applied to solvents with very low extraction capacity or very dilute carrier solutions.

In a paper by Draxler, et. al [62] written on the separation of metal species by ELM, the application was tested on wastewater streams. An ELM configuration was used to recover zinc from viscous wastes at a pilot plant. The ELM was prepared by emulsifying the stripping agent in the liquid membrane phase, and then dispersing the primary emulsion in the wastewater to be treated. A stabilizing surface-active agent was added to the membrane phase. Some issues that were overcome during the testing phase was that the emulsion had to be both stable and have the ability to be split in order to recover the metal ions from the inner phase. Some attempts had

been made to empty this phase without splitting, but it is only possible in special cases. It was found that by increasing the frequency of the electric field there was an improvement in the effectiveness of emulsion splitting.

It was also discovered that water can limit the amount of metals that can be absorbed by the emulsion. The issue of water transport can be eliminated by using surfactants and diluents. In an ELM process it might be necessary to reach equilibrium numerous times for complete separation to be reached.

The experimentation found that zinc, copper, cadmium, and lead can be separated down to concentration levels that are accepted by most environmental agencies. This was not found to be true for nickel and chromium (VI) due to the fact that the residence time in the column in which the tests were conducted was not long enough for nickel separation and high amounts of sulphate ions interfere with chromium concentration reduction. Sulphate transport is negligible when there is high chromium concentrations, but becomes dominating when chromium concentrations are low.

The experiments conclude that the process of liquid-membrane permeation has become an industrial scale process, and a number of pilot plants have proven its feasibility for the separation of certain metals. Draxler et. al (1988) [62] indicates that wastewater treatment using ELM is a very promising field due to the fact that the separation of many metals is as good or better than other processes and the metals involved do not have to be disposed of, but can be recovered. The importance in the selection of surfactant can lead to enhanced stability, increased mass transfer, reduction in the transportation of water, decomposition of extractant and resistance to bacteria. The development of new and improved extractants will enhance selectivity and allow ELM to become an industry standard for dilute waste treatment.

Supported Liquid Membranes

Supported liquid membrane (SLM) are membranes that are impregnated in the pores of a microporous polymeric filter. The membrane can be a variety of geometries including a flat sheet or hollow fiber membrane. The large exchange area available with the hollow fiber SLM yields rapid transport.

Supported liquid membranes in combination with selective carriers for the transport of components of a mixture is becoming more effective but there are very few examples of this technology in large-scale industrial applications. This can be explained by problems related to the performance of the membranes including a short life span (since carrier and solvent are lost to the feed or strip solution by dissolution and micelle formation). Rate of loss depends on the process conditions. The stability of the membrane can be increased by placing a thin polymer layer on top of the liquid membrane [53].

Marchese, et. al (1995) [61] discuss the transfer and separation of Co^{2+} and Cu^{2+} ions across a flat sheet supported liquid membrane containing Alamine 336 as the mobile carrier dissolved in kerosene solvent. The presented results indicate that both the Alamine composition in the organic solution and the hydrochloric acid concentration in the feed solution had an effect on the metal transport. It was found that a maximum flow of these ions was achieved at 50% Alamine in the diluent. Nickel (Ni^{2+}) was not transported through the range of the experimental conditions. The results of the metal liquid-liquid extraction percentage (%E) as a function of the amount of hydrochloric acid is shown in 4.10.

Percent extraction (%E) is defined as:

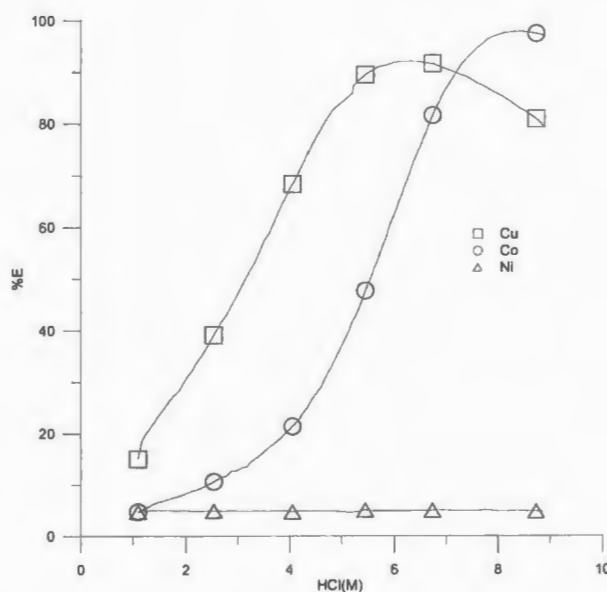


Figure 4.10: Extraction of Cu^{2+} , Co^{2+} and Ni^{2+} with Alamine 336 vs. HCL concentration Using a SLM [61]

$$\%E = \frac{[Me]_{org}}{[Me]_{org} + [Me]_{aq}} * 100 \quad (4.21)$$

where $[Me]$ is the concentration of a metal ion of choice. A maximum ion extraction took place at approximately 5 M of HCl and 9 M of HCl for Cu^{2+} and Co^{2+} respectively. The different behavior of the metals was explained by the formation of stable anionic complexes of the type MeCl_4^{2-} as explained by the following reaction:



From the experiments conducted, copper and cobalt were extracted into the organic phase by the anionic metal complex with protonated amine in the hydrochloric acid medium. Stripping was achieved with distilled water. This particular experiment

shows that with the proper selection of HCl concentration in the feed solution there is an associated selective separation of the metals that are involved.

4.3.1 Dialysis / Electrodialysis

Dialysis exploits the difference in diffusion rates of molecules through the membrane to separate components from solutions. This process is generally applicable to solutions where it is desirable to remove or isolate molecules with an appreciable difference in molecular size (their diffusion rates are very different).

Electrolytic membrane dialysis is a technology that was created in a response to the demand for a system that will clean up relatively small quantities of water contaminated with ionic matter and separate the dissolved species as necessary. Electrodialysis is a possible method for selectively removing ions by size and charge from contaminated solution.

Using direct current electrodes on opposite sides of the membrane it is possible to effectively transport charged particles of small sizes through the membrane at an increased rate. The anode is immersed in the permeate and the cathode is in the retentate. This system causes the anions of small sizes to migrate across the membrane toward the anode and therefore causing a separation from the original solution. It is possible to reverse the flow which will cause the cations to flow across the membrane in the opposite direction. The DC electric field improves on the filtration by using the membrane to hold back ions of one charge, while ions of the opposite charge are encouraged to pass under the influence of the electric charge. The electric field influences the distribution of ions by altering the neutrality rule of the chemical species. With time, the efficiency of the membrane decreases due to pore plugging or blinding

of the membrane. It is necessary to use a cleaning chemical or backwash to avoid this issue.

A bipolar membrane (BM) process is an example of a membrane that consists of a layered ion exchange structure composed of a cation selective membrane (with negative fixed charge) and an anion selective membrane (with positive fixed charge). This process is used for the separation of monovalent and divalent ions. BMs are considered to be a simple, energy saving, and environmentally friendly technology.

Xu (2001) [59] describes the use of a bipolar membrane for the removal of copper from cupric solution (solution in which copper is present in its lowest proportion) using electro-extraction and back-extraction techniques. As shown in Figure 4.11 the feed containing the copper rich solution enters compartment 1 and the ion exchange resin is filled in compartment 2 and 3. When a voltage is applied, cupric ions and other cations are transported through a cation membrane from compartment 1 to 2 where it is selectively extracted under the weak base condition that is controlled by the water splitting rate (electro-extraction stage). The copper rich organic phase is circulated to compartment 3 where back-extraction takes place and cupric ions are released into compartment 4 under the conditions of acidity produced from water dissociation. The result is a copper rich aqueous solution phase contained in compartment 4. This process operates by a combination of ion exchange, extraction, and water dissociation.

In this particular system, the ion exchange resins between the ions and the organic phase increases the conductivity of the organic phase therefore lowering the operational voltages required.

In Figure 4.12, Cobalt (Co^{2+}) and Nickel (Ni^{2+}) separation is accomplished through the use of a bipolar membrane electrolytic cell stack (left side) and a conventional

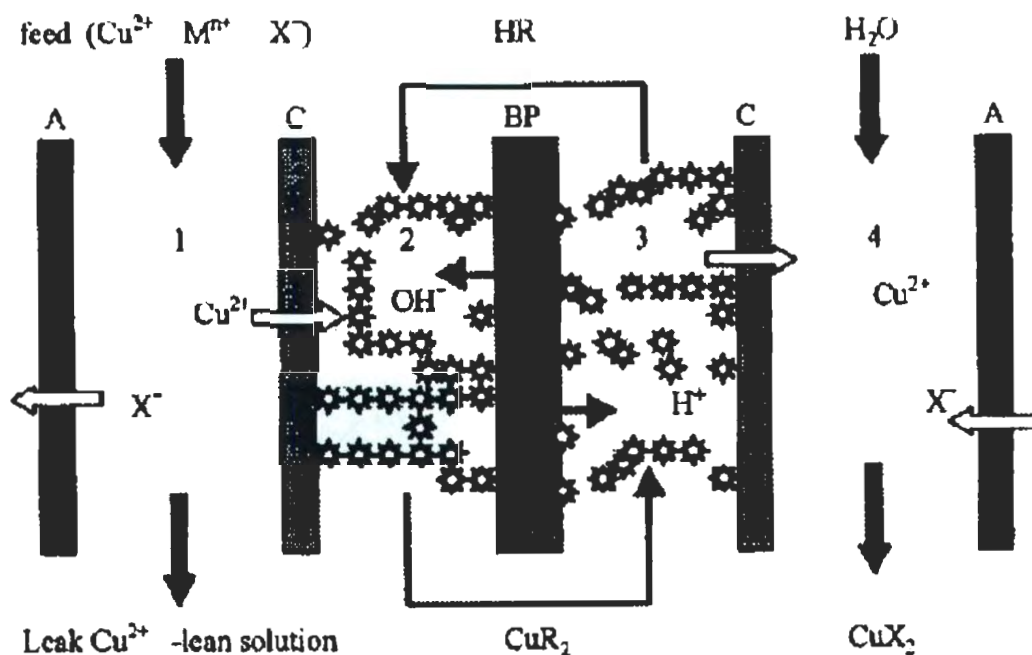


Figure 4.11: Bipolar Electro-Extraction Process for Separation of Co^{2+} and Ni^{2+} [59]

cell stack (right side). The Co^{2+} and Ni^{2+} mixture is fed into compartment 2 of the left cell while the complexing agent (HR) is added to compartment 3. When a voltage is applied, both metallic components join with the complexing agent in the third compartment due to the induced potential difference. Formation of the NiR_2 complex is more probable than the CoR_2 complex, thereby allowing the Co^{2+} to be transported through compartment 4 and stored in compartment 5. The NiR_2 complex is transported to compartment 4 on the right side from compartment 3 on the left where the complex agent is recovered by ions created from water dissociation. Once the agent is recovered and recycled, released Ni^{2+} is transported to the right cell into compartment 5. System neutralization is achieved by using a basic solution leading to a high concentration of Co^{2+} and Ni^{2+} in compartment 5 of the left and right cells, respectively. Mo et al. indicate that the concentration ratio Co:Ni can

reach 20:1 in the left cell and 1:20 in the right cell if the feed contains equal molar concentration of 0.15 mol/L and the current efficiencies for both electrodialysers are above 70%.

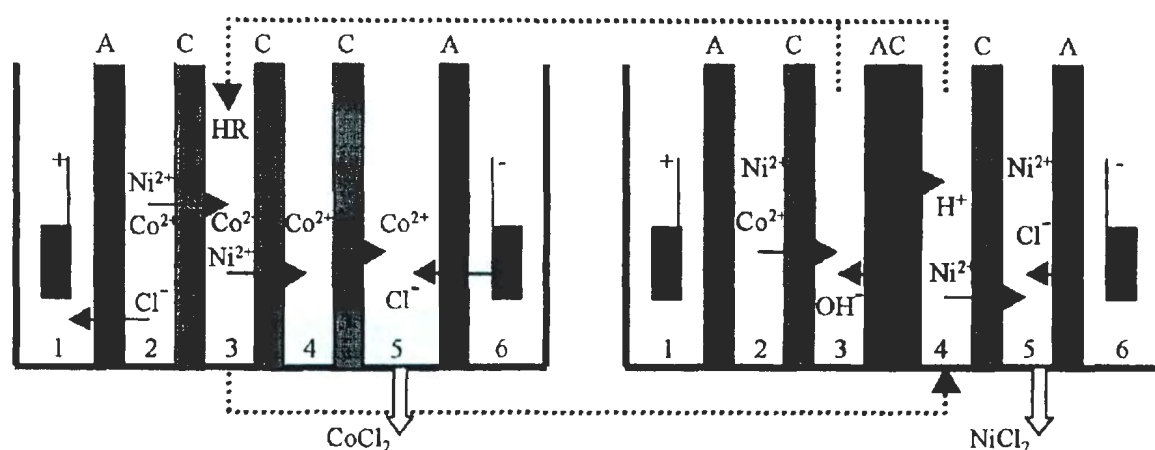


Figure 4.12: Use of integrated BM and Absorption unit for removal of Co^{2+} and Ni^{2+} ions [59]

An effective means to recover heavy metals and enhance product purification is to use a BM membrane. This method increases selectivity of a component(s) in the effluent where the optimal adsorbent is utilized. Filtration is a required pretreatment to remove insoluble materials, sludges, etc. Advantages to the use of BMs include the reduction of waste streams, obtains the product in a purified and concentrated form, and performs extractions not possible through conventional techniques (such as the separation of ions with the same valence and sign).

4.3.2 Reverse-Osmosis

In osmosis, transfer of the solvent occurs from a dilute to a more concentrated area across a membrane which impedes the transfer. Solute separation and permeate water flux is a function of membrane material and the structure of the barrier layer. When

enough water passes through a semi-permeable membrane from the side with low to high solvent concentration equilibrium is achieved. At equilibrium the pressure drop across the membrane is equal to the osmotic pressure difference. Reverse osmosis (RO) occurs when a pressure difference greater than the osmotic pressure is applied and causing flow to reverse.

RO typically occurs at ambient temperature and does not require a phase change. This makes it appealing for use with unstable chemicals. The following experimental equation represents the osmotic pressure π for dilute water solutions:

$$\pi = \frac{n}{V_m} RT \quad (4.23)$$

where n is the number of kgmol of solute, V_m is the volume of pure solvent, R is the universal gas constant and T is the temperature.

As the concentration of the solution increases the behavior of the osmotic pressure deviates according to an osmotic coefficient ϕ (the ratio between the actual osmotic pressure and the ideal osmotic pressure). Numerous membranes are available for industrial use with reverse osmosis theory. Examples include the cellulose acetate membrane (used in desalination processes), and the synthetic aromatic polyamide membrane known as “Permasep”[52]. Each membrane type has its own advantages and drawbacks which cater to specific applications.

For diffusion through a membrane in a reverse-osmosis process the following equation governs the transport of the solvent:

$$N_w = \frac{P_w}{L_m} (\Delta P_h - \Delta \pi) = A_w (\Delta P_h - \Delta \pi) \quad (4.24)$$

where N_w is the solvent flux, P_w is the membrane solvent permeability, L_m is the membrane thickness, A_w is the solvent permeability constant, ΔP_h is the hydrostatic pressure difference, and $\Delta\pi$ is the osmotic pressure difference between the feed and the production solutions.

The following equation governs the transport of the solute:

$$N_s = \frac{D_s K_s}{L_m} (c_s - c_2) - A_s (c_1 - c_2) \quad (4.25)$$

where c_1 and c_2 are concentrations of the solute upstream (1) and downstream (2) of the membrane.

A steady state material balance for the solute diffusing through the membrane and the solute leaving in the product solution yields:

$$N_s = \frac{N_w c_2}{c_{w2}} \quad (4.26)$$

where c_{w2} is the solvent concentration in the product stream. The solvent flux rates depend on the pressure difference where the solute flux depends on the concentration difference.

One type of a reverse osmosis process is nanofiltration which allows for the possibility of selectively separating hazardous components. Reverse osmosis is a membrane process which has been popular in water treatment, separation processes in the food and beverage industry, and in the pulp and paper industry. Reverse osmosis has shown potential in treatment of low pressure dilute aqueous wastes that have high fluxes over a wide range of pH levels [52].

In addition to the general advantages of membranes, reverse osmosis offers a few more advantages. These processes are generally simple to design and easy to operate. It can be integrated into another process (such as ultrafiltration) to become a hybrid process. Also, processes with high osmotic pressures and high concentrations of monovalent salts, reverse osmosis becomes the ideal solution [52]. Separation using the reverse osmosis method does not require phase change which leads possible energy savings and flexibility in design. Ideal RO membranes should resist chemical and microbial attack, and the mechanical characteristics should not change after long term operation. Compared to processes such as incineration for waste treatment, membrane processes can provide up to a 50 fold decrease in waste volumes.

Technological improvements have increased the number of applications of reverse osmosis in industry processes. New materials are more pH, temperature, and chlorine resistant as compared to cellulose acetate membranes. An increased flux performance is realized through the use of thin-film composite (TFC) membranes which also enhances separations of organics under lower operating pressures. RO membranes are available as one polymer (asymmetric design) or the TFC structure [52, 36].

RO membranes have very small pore structure, with the pore diameter ranging from approximately 0.5nm-1.5nm. Due to the small size of the pores, only the smallest molecules can pass through the membrane along with the water.

The important operating variables for RO are feed flow rate and concentrations of dissolved solutes, types of solutes, transmembrane pressure ΔP , temperature (T), pH, and concentration of suspended solids. The RO process is evaluated in terms of three parameters: observed solute rejection R_r , water flux J_w , and water recovery r .

Observed Solute Rejection, R :

$$R_r = 1 - \frac{c''}{c'_b} \text{ or } 1 - \frac{c''}{c'_c} \quad (4.27)$$

Intrinsic Membrane Solute Rejection, R' :

$$R' = 1 - \frac{c''}{c'_w} \quad (4.28)$$

Solvent or Water Recovery (for batch systems), r :

$$r = \frac{\sum J_w A_x \Delta t}{V_o} \quad (4.29)$$

Solvent or Water Recovery (for continuous systems), r :

$$r = \frac{J_w A_x}{Q_i} \quad (4.30)$$

where J_w is volumetric, mass or molar permeation rate / membrane area

Although not measurable, the chemical potential gradients across the membrane represent the thermodynamic driving forces in solvent and solute transport through RO membranes. Alternatively, the driving forces are related to differences in chemical concentration and pressure differences across the membrane.

Bi-polar membranes consist of two layers in series, one layer having a fixed positive charge and the other a negative charge. Tüsrü et al. [60] investigated the use of bi-polar membranes (BMs) in reverse osmosis for the separation of ions with different valencies. For ions with equal valence, the BM process is ineffective. Through the use of the bi-polar reverse osmosis membranes it is possible to separate divalent ions from

monovalent ions for both cations and anions. Figure 4.13 part a) shows the separation by a negatively charged monopolar membrane, while (b) shows the bipolar membrane application. The driving force in reverse osmosis is pressure difference causing a volume flux through the membrane. In RO the solutes that are larger than pore size of the membrane are rejected, while smaller particles are allowed to permeate through the membrane. A repulsive force on anions and an attractive force on anions occur with the negative charged membrane. Overall, a negatively charged membrane has good selectivity toward mono- and divalent anions and poor selectivity toward mono- and di-valent cations.

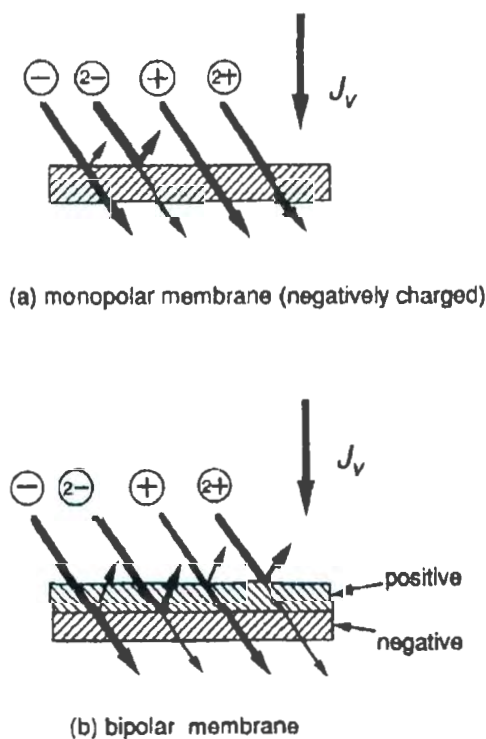


Figure 4.13: Rejection model of mono- and bi-polar membrane in RO [60]

The ultimate goal of bi-polar membranes is to separate mono and divalent anions and cations through repulsive or attractive charges. Due to the bi-layer structure divalent cations are strongly repulsed by positively charged first layer and divalent anions are

repulsed by the negatively charged second layer. In the meantime the mono-valent anions and cations permeate through the membrane due to lower repulsive forces.

Benito and Ruiz [68] apply reverse osmosis in the electroplating industry. In an industry that requires an intensive water supply, the results indicated that between 75-90% of the water could be recovered and nearly all of the metals in the permeate could be removed through reverse osmosis.

Ozaki et al. (2002) [65] conducted experimental studies on the use of aromatic polyamide (ES 20) ultra-low-pressure reverse osmosis membrane (ULPROM) for separating divalent metals from bulk solution. Pressure, feed concentration, pH, and the presence of other ions such as Ca^{2+} and Mg^{2+} were explored for effects on performance. The experiments were conducted on a synthetic wastewater and wastewater from a heavy-metal industry. The results indicate that rejection increases with increased feed pressure increased pH levels. Results indicated that 95% rejection of heavy-metals for the ULPROM tested can be achieved and therefore can be applied in industrial applications for recovery of heavy-metals and reclaiming wastewater.

The removal of a substance is occasionally measured in terms of rejection, which is the ratio of the quantity of the targeted substance in the retentate to that of the feed. It is expressed as a percentage of the feed concentration and can also be written in terms of mass transfer coefficients:

$$Rejection(R) = 1 - \frac{K_S}{[K_W(\Delta P - \Delta\pi)(2 - 2f_w)/(2 - F)] + K_S} \quad (4.31)$$

where f_w = fraction of water recovery = Q_p/Q_f , (Q_p = quantity of permeate and Q_f = quantity of feed), K_S = solute mass transfer coefficient, K_W = water mass transfer

coefficient, ΔP – transmembrane pressure gradient, $\Delta\pi$ – transmembrane osmotic pressure gradient.

Since this is a pressure driven membrane, an increase in transmembrane pressure will cause an increase in the flux and the subsequent rate of rejection. Optimal pH range for highest rejection is 7-9. The presence of co-ions will decrease the rejection which is observed with wastewater solutions [65].

4.3.3 Ultrafiltration

Membranes used for ultrafiltration are similar to the membranes used in reverse osmosis. The membrane is comprised of a thin skin reinforced by a porous layer for strength. The equipment is similar to reverse osmosis. Ultrafiltration is driven by pressure differential and molecular size whereby larger solute molecules are impeded by the membrane. Recommended practice suggests that if the molecular size between the rejection molecules the remaining molecules differ by a factor of 10 then ultrafiltration can be applied successfully [55].

The small pore size of the ultrafiltration membrane provides a filter for a given feed stream. If the impurity is too small the process may be unfeasible. In an effort to improve the ultrafiltration process where impurities are very small, it has been proposed to utilize water-soluble ligands to form a complex with the impurities thereby increasing their size to be larger than the pore size. This process has been particularly successful in the removal of metals from wastewater to meet stricter environmental policy and economically reduce fresh water consumption.

Atamaneko, et al [67] highlight combining sorption and ion exchange processes with either ultrafiltration or reverse osmosis. Through experimentation, specific sorbents

were pretreated to enhance the separation. The membranes used were OPAN-KN (reverse osmosis) and UPM-20 (ultrafiltration). It was determined that for a feed of 25 ppm Co(II) and 1 g/l of the sorbent montorillonite, OPAM-KN yielded a retention coefficient for Co(II) of 0.97-0.98. When the sorbent KU-2-8n was used a retention coefficient of 0.91 and 0.92 was found. Compared to the initial retention coefficient of 0.82 the use of sorbents enhances the process dramatically. The montorillonite had no effect on the ultrafiltration process but when used in association with the KU-2-8n the results were positive.

Tavares, et al. performed a study indicating that 54% of Fe and 50% of chemical oxygen demand (COD - an indirect measure of organic material in the solvent) could be removed with a relatively short contact time (24 hours). After 120 hours, up to 80% of Fe and 53% of the COD was removed. pH level plays a significant role in the effectiveness of this process. It was determined that the optimal pH level for metal removal was approximately a pH of 4. The combination of ultrafiltration and complexation has been shown to greatly improve the removal of metal ions [66].

The flux equation for ultrafiltration is similar to reverse osmosis with the exception that the osmotic pressure difference can be neglected since ultradiffusion does not allow passage of the macromolecules of the solute, and the concentration of the large molecules is generally small [54]. The solvent flux equation can be written as:

$$N_w = A_w (\Delta P) \quad (4.32)$$

This equation holds for low pressure drops and dilute solutions.

Ultrafiltration has been shown to be a promising technique for trace metal removal from industrial wastewater. The advantage of using this method includes the high

selectivity available due to binding that takes place between the ions and the polymers as well as the low energy requirements.

4.3.4 Microfiltration

Microfiltration is similar to both reverse osmosis and ultrafiltration in that it is pressure-driven but it works to remove particles which range from $0.02\ \mu\text{m}$ to $10\ \mu\text{m}$ in size. The large particle size generally means that osmotic pressure can be neglected. Material and equipment selection for microfiltration is typically application specific.

The flux equation for a microfiltration membrane can be written as:

$$N_w = \frac{\Delta P}{\mu(R_m + R_c)} \quad (4.33)$$

where μ is the viscosity of the solvent, R_m is the membrane resistance, and R_c is the cake resistance.

Another possible modeling procedure is the use a cross-flow microfiltration model. This model is similar to that of the ultrafiltration or reverse osmosis model. The bulk solution is parallel to the membrane and not perpendicular through the membrane. This type of process is efficient in controlling problems such as cake build-up and concentration polarization.

4.4 Conclusions

For each membrane technology a detailed analysis can be conducted to determine feasibility. A general overview of membrane technologies has been presented to provide a fundamental base to build upon for future research. Upon further research, it may be determined that one specific membrane technology may be better suited for INCO's waste stream.

Chapter 5

Biotechnology

The expanding world demand leads to the development of lower grade ore bodies. New technologies are surfacing to reduce the capital and operating costs to treat and handle the dilute wastes created by these processes. During the past two decades many advancements have been made to help mineral processing, remediation and reclamation. Many forms of compounds found on mineral processing sites are harmful to human health and the natural ecosystem [77]. It is not uncommon for these compounds to reach natural waterways and spread throughout the ecosystem in a diluted form. Natural waters polluted by mineral wastes are often contaminated with heavy metals. These metals can be independently toxic or toxic when combined with other ions. Treating polluted areas where the contaminants are present in low concentration can be expensive and difficult. “It (is) known that many microorganisms can remarkably concentrate heavy-metal ions from aqueous solution”[79]. Some microorganisms have been found to possess the selectivity and binding properties that offer an economic and environmentally sound solution to the cleanup of these metals [77]. These organisms are used more commonly in the remediation of waste in the mineral processing industry than ever before [79]. In an era where environmental

regulations are tightening it is becoming more important for industry to find waste treatment solutions that are more efficient, economic, and effective.

Treating dilute waste streams is challenging because the volumetric flow rate of the effluent stream is generally high whereas the concentration of heavy-metal ions are low. Targeting specific ions in a medium with a high flow rate poses technical and economical challenges. Microorganisms possess the selectivity and cost effectiveness necessary to make biotechnology a viable solution in the removal of heavy-metals from dilute aqueous streams [79]. It is also possible to utilize this technology to recover additional metals, previously uneconomical, from the waste streams.

Of increasing importance is the identification of biological strains that are effective in the removal of desired heavy-metal ions under specific environmental conditions. The behavior of the microbes is affected by the presence of competing ions or different acidic levels, thus it is important to associate the microbe with its optimal conditions such that it may perform its specific duties to its maximum potential [79].

Scientists are searching for a bug that will revolutionize the mining industry. Microbes have been found that process ores of copper, gold, lead, zinc, and silver near hydrothermal springs. These microbes have evolved in extreme environments and can withstand conditions unlike microbes which exist at ambient conditions. Microbes that subsist on sulfides and other compounds in an environment that has high temperature, pressure, salinity, acidity and toxicity exist and possess some of the characteristics necessary to receive interest from researchers. The extreme conditions force the metabolism of these microorganisms to have accelerated rates. Current studies focus on ways to develop microbes to perform under controlled and more ambient conditions. To date the process is inexpensive but slow. Many companies are

using this technology in applications such as treating waste heaps[72].

It is also important to learn how to mathematically model these bioprocesses. In order to optimize the process it is important to understand not only what factors affect the process, but to what degree[73].

Biotechnology can be categorized into three sectors consisting of biomining (including biooxidation and bioleaching), bioremediation, and biosorption. At present, biomining and bioremediation are active in full scale operation and biosorption has yet to be proven to be viable at a commercial level. The majority of research conducted has concentrated on biooxidation and bioleaching of sulfides[73].

5.1 Types of Microorganisms

Applications for biotechnology have surfaced in the treatment of process effluents and drainage waters containing traces of metals and acids. The identification of organisms which are involved in processes such as bioleaching and biooxidation is paramount in developing the technology. Research is being conducted to genetically engineer these organisms to better suit their purpose.

There are many types of organisms involved in biotechnology. Most organisms possess certain traits which allowing them to perform specific mineralogical tasks. Unfortunately, no one microorganism possesses the traits required to treat all effluent streams, therefore care must be taken in choosing the appropriate microorganism. There are three microorganisms which are most common and frequently documented.

Thiobacillus ferrooxidans was first documented in 1947. It has been shown to leach metals from sulfides effectively. Considerable effort has been put into developing new

strains of this microorganism. However, this particular microorganism is genetically unstable and thus difficult to attain repeatability in experiments and consistently create effective strains. It is still very commonly used and is a well known sulfide reducing bacteria [86].

Leptospirillum ferrooxidans is an iron oxidizing microorganism. The feature which makes this organism popular is its ability to survive and perform at elevated temperatures. It reaches its maximum potential within the temperature range of 45 to 70°C at low pH levels [83].

Thiobacillus thiooxidans is a sulfur oxidizing microorganism which also performs well at elevated temperatures (45 to 70°C). It also has the ability to withstand higher pH levels and high hydrostatic pressures.

Other microorganisms exist and have the potential to treat effluent streams. For example, biomass from aquatic plants has shown the potential to be useful in biotechnologies. Different species of algae and non-living matter from red and brown seaweed has recently been the subject of research [70].

5.2 Biomining

Biomining focuses on processes traditionally involved with conventional mining. Typical tasks performed by microorganisms include bioleaching and biooxidation.

Table 5.1 lists factors influencing mineral oxidation and mobilization by microorganisms [80]. Typical physiochemical parameters affecting mineral oxidation and mobilization in a bioleaching environment include temperature, pH, oxygen content, light, nutrient availability and pressure. Microbiological conditions affect the process

of bioleaching in several ways. The density of the organisms and spatial distribution will affect the rate of reaction. The microorganism's tolerance to the presence of metals may also affect metal mobilization. Thirdly, the properties of the minerals to be leached have an impact. Microorganisms may prefer minerals to have a certain grain size or amount of surface area to contact. Porosity of the treated medium can alter the degree in which the oxidation takes place. Finally, the type of processing will also affect the mineral oxidation and metal mobilization. The leaching mode, pulp density, stirring rate, and heap geometry all have different advantages and disadvantages.

Three examples of typical biomining applications are irrigation based, in-situ applications, and stirred tanks. Irrigation based bioleaching involves dump / heap leaching where large boulder-sized pieces of ore are put in a mound and exposed to biomaterial and irrigated with sulfuric acid. In-situ bioleaching is used in spent inoperative mines where the mine is fractured and fed acid liquors containing specific bacteria through the fractures. This liquid is collected and the dissolved metals can be recovered. The process of using stirred tanks offers the most controlled environment since it is man made.

5.2.1 Bioleaching

Bioleaching is “the dissolution of metals from their mineral source by certain naturally occurring microorganisms” [80]. It refers to the conversion of solid metal ions into a water soluble form. Once the metal has been extracted, solvent extraction and electrowinning can be used to recover the product from solution. The microbes can liberate metals in one of three ways [80]:

- the formation of organic or inorganic acids

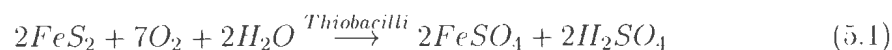
Table 5.1: Factors Influencing Mineral Oxidation and Mobilization by Microorganisms [80]

Factor	Parameter
Physiochemical parameters of a bioleaching environment	temperature pH redox potential water potential oxygen content and availability carbon dioxide content mass transfer nutrient availability iron(III) concentration light pressure surface tension presence of inhibitors
Microbiological parameters of a bioleaching environment	microbial diversity population density microbial activity spatial distribution of microorganisms metal tolerance adaptation abilities of microorganisms
Properties of minerals to be leached	mineral type mineral composition mineral dissemination grain size surface area porosity hydrophobicity galvanic interactions formation of secondary minerals
Processing	leaching mode (<i>insitu</i> , heap, dump or tank leaching) pulp density stirring rate (in case of tank leaching operations) heap geometry (in case of heap leaching)

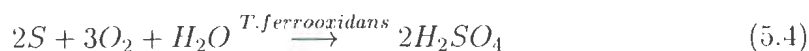
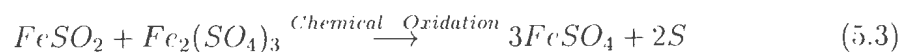
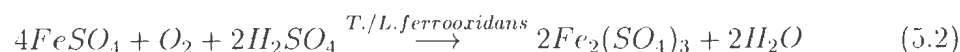
- oxidation or reduction reactions
- excretion of complexing agents

Once mobilized the metals can be leached by direct or indirect mechanisms. The direct mechanism requires close contact between the microorganisms and the reduced minerals. For the indirect mechanism, it is necessary to have an electron carrier such as ferric iron (Fe^{3+}) originating from the microbial oxidation of ferrous iron (Fe^{2+}) compounds present in minerals [80].

An example of the direct mechanism is the oxidation of pyrite:



An example of the indirect mechanism involving pyrite is given next:



A common application of bioleaching is in the removal of copper from industrial wastes. The microorganism utilized for this purpose is thiobacillus ferrooxidans. Under optimal conditions between 61 and 96% of copper can be removed [84]. Copper

can be produced from mining wastes and low grade ores by bioleaching methods for an estimated one-third to one-half the cost of copper produced from high grade flotation concentrates in conventional smelting [86].

Bioleaching is used in biohydrometallurgy as an economic and environmentally responsible way to improve the process [87]. Microorganisms can be autotrophs, mixotrophs, or heterotrophs. What distinguishes these microbes is where they obtain energy and nutrients. All forms of microorganisms obtain energy from oxidation but autotrophs receive carbon from carbon dioxide. Mixotrophs, on the other hand, obtain carbon only partially from organic compounds. Heterotrophs obtain carbon from the assimilation of organic compounds.

Autotrophs are considered the most desirable because of their ability to grow in the absence of organic matter. Unfortunately they tend to grow at a slower rate compared to the other two types. Heterotrophs require one or more organic nutrient(s) for energy and carbon consumption. They have potential to be used where metal sulfide ores contain a large amount of acid-consuming constituents exist. This typically causes the pH of the system to fluctuate and thus acidophiles are unlikely to grow well [85].

Some bioleaching processes are currently in existence at a commercial level. For example, natural biological sulfur and nitrogen cycles offer bioconversions that are successful at the industrial scale. Waste can be converted (under ambient conditions) to a reusable product or harmless by-product [87].

5.2.2 Biooxidation

Biooxidation is very similar to bioleaching with a few subtle differences. The primary difference in biooxidation is that it leaves the metals in a residue instead of in solution [81]. Biooxidation has been identified as a potentially low cost way to extract metals such as copper, lead, zinc, nickel, silver, gold, and uranium while limiting the negative effects of traditional processing. It is an oxidation process catalyzed by bacteria and generally occurs at near ambient conditions [71]. As of March 2005 there were 22 biooxidation plants in operation, 8 pending and 6 closed [75]. An example of biooxidation is the dissolution of pyrite and arsenopyrite which allows for the liberation of precious metals by cyanidation[73].

Certain conditions can accelerate the oxidation process. Typically, a higher oxidation rate is found by lowering the pH and elevating temperatures in the presence of high concentrations of dissolved metals. Unfortunately this limits the type of microorganism that can be used. Microorganisms that typically function well under these conditions are single-celled and prokaryotic types. These cells tend to live in highly acidic liquors. Most active strains of bacteria with these characteristics have yet to be classified[73].

5.3 Bioremediation

Bioremediation uses microorganisms in the remediation of polluted soils or waters. It involves the use of biological agents to reclaim soils and waters polluted by substances hazardous to human health, the environment, or both. It is an extension of biological treatment processes used to treat wastes in which microorganisms biodegrade en-

vironmental pollutants. Although not applicable in every situation, microbiological processes can be used to remediate acidic wastewaters and be an economic way to treat a range of sulfide ores and concentrates [75, 73].

Active bioremediation offers system control of the separation and recovery of metals.

At full scale, only compost bioreactors and constructed wetlands have been used. Although the maintenance costs are low and solid phase products are retained, they can be expensive to install, perform inconsistently, and require large amounts of land. The potential for the reuse of metals from waste streams by recovery using this method is lower than other processes [73].

One successful bioreactor in the Netherlands has been in operation since 1992. This bioreactor uses a Thiopaq process with two distinct microbiological steps: the conversion of sulfate to sulfide by sulfur reducing bacteria and the conversion of hydrogen sulfide to sulfur using sulfur oxidizing bacteria. Both processes are used to treat zinc rich wastewater [73].

High rate bioreactors also operate with smaller volumes but offer improved process control and higher conversion efficiencies. Globally, approximately 2000 bioreactors exist and are used mostly in the treatment of high strength industrial wastewater [87].

5.4 Biosorption

Biosorption is considered an alternative to traditional techniques to treat diluted solutions containing heavy-metals. It has been used in experiments to reduce the toxicity where traditional methods become less economically feasible (when metals

are present in concentrations less than 100 mg/l) [76]. Biosorption is a biotechnology that can occur in two ways. It can occur by adsorption of ions on the cell surface (accumulation or precipitation) or as bioaccumulation within the cell [78].

Adsorption involving biomaterial has an initial fast and reversible metal binding reaction. Biosorbents are chosen based on the specifics of the application. Some have broader ranges of application and bind with heavy-metals while others target specific ions [74]. Accumulation is typically slower, and irreversible and has an ion-sequestration step. This bioprocess has been applied to treat wastes with metals such as lead, zinc, and copper (including toxic materials such as metaloids and radionuclides).

Aquatic plants, both living and non-living, have been found to act as efficient heavy-metal accumulators and are a focus of considerable research [82]. The major difference between using living versus non-living microorganisms is the nutritional requirement is higher for living microorganisms. In some cases the rate of reaction can be directly or indirectly tied to the metabolism rates of the microorganisms and can therefore be controlled [88]. When choosing a biotechnology it should be noted that certain algal species may be more effective and selective than others for removing particular metal ions due to the difference in cell wall composition [3]. Figures 5.1 and 5.2 depicts typical biosorption processes in use for remediating toxic metal pollution. Examples include packed-bed reactors, fluidized-bed reactors, Rotating-disk reactors, sludge-blanket bioreactors and artificial wetlands/stream meanders.

The plants that are used in biosorption are commonly found in ponds and lakes. Generally these plants absorb nutrients from the surrounding water. They are stratified among the lower depths of the body of water and along the water's surface. The

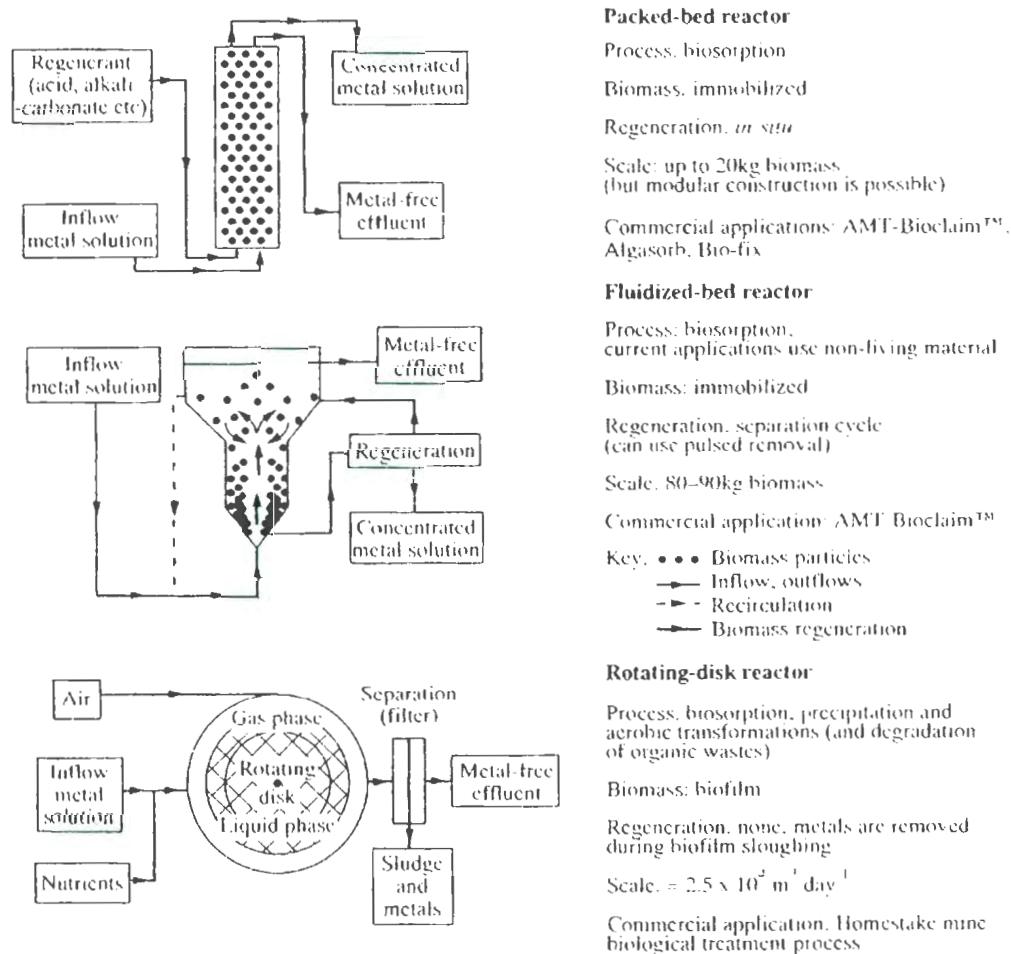


Figure 5.1: Examples of Typical Biosorption Processes - I [88]

cell wall components which possess the metal binding capability are carboxyl groups those with high chitin content (a polymer of N-acetyl glucosamine) [88]. Studies have shown that the kinetics of adsorption by any biological material can be represented by the first-order Lagergren equation [82]:

$$\ln (q_e - q_t) = \ln (q_e) - k_t \quad (5.5)$$

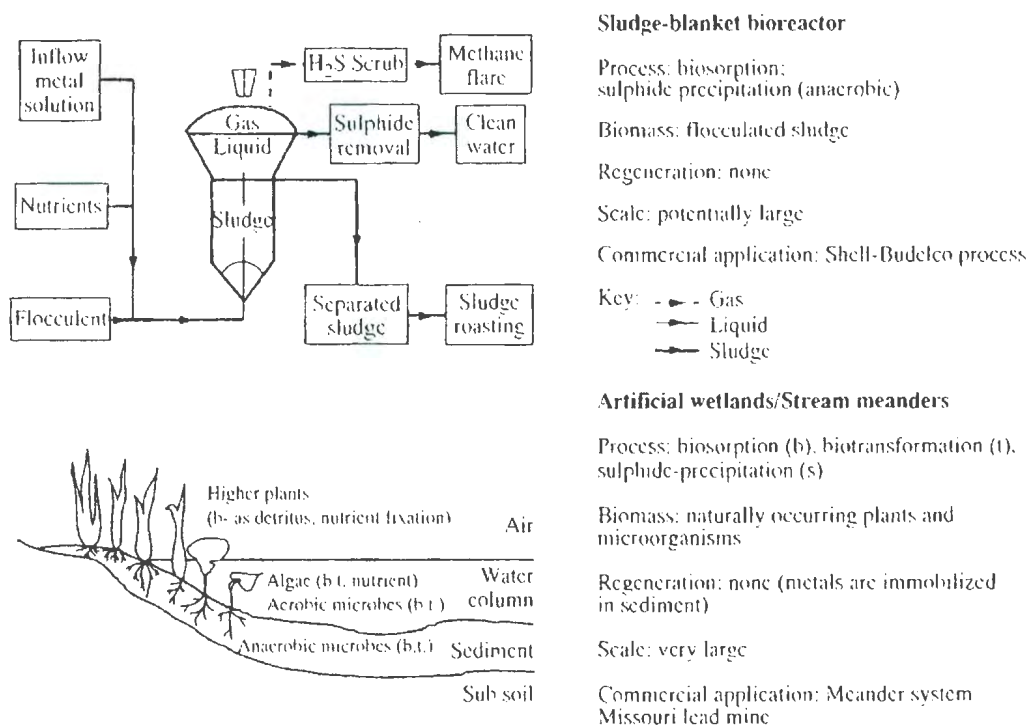


Figure 5.2: Examples of Typical Biosorption Processes - II [88]

The second order equation may provide a more accurate representation:

$$\frac{t}{q_t} = \left[\frac{1}{2} k' q_e^2 \right] + \frac{t}{q_e} \quad (5.6)$$

where q_e is the mass of metal adsorbed at equilibrium; q_t is the mass of metal adsorbed at time t ; k_t is the first order reaction rate constant of adsorption; and k' is the pseudo second order rate constant of adsorption. This relationship has proven to be a reasonable fit for the aquatic plant *ceratophyllum demersum* (coontail or hornwort) for the treatment of copper, zinc and lead [82].

Four factors have been identified as having a significant impact on the degree of success of a biosorption process. First, temperatures outside the range of 20°C to

35°C have positive impacts on the biosorption process. Second, the pH affects the activity of the functional groups and competition for metallic ions (which has the most influence of the four factors). The concentration of biomass in solution also influences uptake. The lower the biomass concentration the higher the uptake to an optimal point. Finally, the removal of a specific metal ion may be influenced by the presence of another. This may be due to competition for the metal binding sites within the biomaterial. Additionally, pretreatment with alkalies, acids, detergents and heat prior to utilizing the biomaterial can greatly enhance the effectiveness of the biosorption process by intensifying metal affinity. Some of the characteristics of biosorption and bioaccumulation are listed in Table 5.2 [3].

One experiment used *Thiobacillus ferrooxidans* as the biosorbent to treat a copper perchlorate $Cu(ClO_4)_2$ solution prepared to simulate wastewater. The copper solution was pretreated with sodium hydroxide and deionized water until the pH was neutral. It was then suspended in sodium perchlorate solution. An agitated tank was used as the experimental apparatus. The results of the experiment confirmed that the most favorable isotherm occurred at a pH of 6 and at a pH of 3 the reaction rate was near zero. The chemical pretreatment caused an increase in permeability of the cellular walls thereby increasing the availability of binding sites. Finally, elevating the temperature from 25 to 37°C increases the capacity by 68% [76].

A similar study focuses on the species *solanum elaeagnifolium* (silverleaf nightshade). The metals in the study target lead, copper, nickel, cadmium, zinc and chromium. Most metals increase binding tendencies to the biomass with an increase of pH up to a level of 5 to 6, with the exception of Cr(IV). Most binding occurs in the first 10 to 15 minutes of the experiment so it is theorized that binding occurs on the cell walls of the plant tissue. It was also found that pretreatment with sodium hydroxide leads

to an increase in capacity. Additionally, the recovery of metals from the biomass was very successful [77].

In comparison with traditional treatment processes, biotechnology has advantages and disadvantages. Biotechnology requires a moderate capital investment since it can take the place of certain non-biological processes and utilize similar equipment. After the capital investment, bioprocesses have very low operating costs. Microorganisms are known to be highly selective allowing for the targeting of metals with low concentrations in effluent streams. They provide an appropriate recovery of metals from low grade ores and waste materials. A third advantage is the simplicity of the procedures and equipment needed which does not require skilled operators. Another advantage in terms of environmental protection, is the fact that bioprocesses are non-toxic. With biotechnology there are no toxic additives and therefore no risk of making a potential environmental situation worse [74]. Finally, microorganisms have the ability to tackle two problems simultaneously which is not possible with a conventional process. Metal ions can be processed and sulfate ions can be reduced and removed in a single operation [3].

Biotechnology also has pitfalls. It has the possibility of having a slow reaction time and a variability in performance. Consistency can be an issue with bioprocessing as the rate of reaction is dependent upon so many variables. This may cause recoveries to be lower than other processes. Finally, although some strains of microorganisms are robust, adaptable and require minimal maintenance, the number of strains available is small. For a given waste stream there is no certainty that a microorganism exists that will satisfy the requirements of the operation [81].

Biosorption experimentation has proven that the technology is viable however it still

needs full-scale testing in order to be regarded as a solution to the treatment of wastewater from industrial processes.

5.5 Conclusions

Future research is required to determine if biotechnology is a viable technology to treat the specific effluent stream from the INCO hydromet process. As a newer technology, there is less historical information available. This makes the research and development costs and risks associated with this technology greater than the other two aforementioned processes. At this stage, elimination of any bioprocess would require additional research and clarification of project parameters (such as risk tolerance).

Table 5.2: Metal Biosorption and Bioaccumulation Characteristics [3]

Feature	Biosorption	Bioaccumulation
Metal Affinity	High under favorable conditions	Toxicity will affect metal uptake by living cells, but in some instances high metal accumulation
Rate of metal uptake	Usually rapid, a few seconds for outer cell wall accumulation	Usually slower than biosorption
Selectivity	Variety of ligands involved, hence poor	Better than biosorption, but less than some chemical technologies
Temperature tolerance	Within a modest range	Inhibited by low temperatures
Versatility	Metal uptake may be affected by anions or other molecules Extent of metal uptake usually pH dependent	Requires an energy source Dependent on plasma membrane ATP (as an energy source) - ase activity; Frequently accompanied by efflux of another metal

Chapter 6

Technology Comparison

This section summarizes the technologies and presents a conceptual methodology for selecting a separation technology.

6.1 Ion-Exchange

The ion-exchange process is a technology that is firmly established, well represented, and demonstrates significant capital investment by industries. Research has been conducted on various fronts to improve process effectiveness, accuracy in predictive models, and the life-expectancy of resins. Analytical representations have been developed and are continuously improving to improve the modeling and prediction of system performance. Resin technology is also evolving which is evident from the growing number of commercially available resins designed to achieve specific results for a number of industrial applications.

When applying ion-exchange technology to any process the choice in resin will have a direct effect of the results that can be achieved. The effectiveness of the ion-exchange system depends on a number of factors. This is advantageous in that adjustments can

be made on details such as resin type, size, shape, process style, flow rate, and pH to improve system operation. Regeneration allows for reuse of the resin beds, increasing the life span of the resins, lowering the operational costs, and reducing maintenance complexity.

There are many options available when choosing a specific type of ion-exchanger. Options include batch, column or fluidized technologies. The optimal choice depends on numerous factors including the service conditions, and the desired end results.

Some limitations to the ion-exchange process include the fact that the presence of interfering ions in the system can have a negative impact on the systems productivity. Separation of closely related ions can pose to be a problem, especially if the resin chosen has a similar selectivity affinity to more than one ion. The ion-exchange process generally needs additional steps to extract the metal of interest from the solution (such as precipitation or evaporation). Temperature, pH and other process conditions will have a direct effect on the systems performance. Occasionally a particle will block the pores of the resin, therefore decreasing its separation performance. This blockage could lead to turbidity in the system creating high pressure drops or channeling of the solution through the bed so that the resins full potential is not achieved.

The ion-exchange technology has proven to be a viable solution to the removal of dilute metals from the waste-waters of industries including mining and electroplating.

6.2 Membrane

Membrane separation is divided into a number of specific technologies that can be applied to various separation requirements. Liquid membranes, electrodialysis, reverse osmosis, and, ultra / microfiltration are all technologies that fall under the umbrella of membrane separation.

Overall membranes are compact and modular, are capital and energy efficient, remove toxic metals substances to low levels, are not complicated, and have high surface area for mass transfer. Membranes are influenced by a number of driving forces including pressure, chemical and concentration gradients. Membranes are available in an extensive array of materials, shapes, structures, and modules that can be chosen for a specific separation goal.

Liquid Membranes have an advantage over other membranes due to their ability to conduct extraction and stripping in one phase. This can also be a disadvantage because of the instability that is caused with the stripping phase which can lead to rupture of the emulsion. As with most separation technologies, it is important to choose the most effective reagent for the particular metal of interest. Temperature, membrane thickness, mixing rate, pH, amount of solute in the feed phase, treat ratio, amount of stripping reagent, volume fraction of internal phase, and presence of ligands in the feed will all have a direct effect on the performance of the membrane. It has been proven that LMs are capable of selective separation and concentration of pollutants from dilute aqueous waste streams and have been applied to heavy-metal recovery. It is capable of reducing metal concentration from several hundred ppm to 1 ppm.

Electrodialysis removes ions based on size and charge. The use of electrodes allows for increased rates of transport to be achieved which leads to enhanced product purification. The effectiveness of this technology is influenced by the electromotive force, amperage, and the particle charge to be removed. Effective adsorbents need to be chosen for maximum extraction results. Electrodialysis reduces waste disposal amounts and generates desired product in a purified and concentrated form. Bi-polar membranes, for example, can perform extractions that are not feasible using some conventional techniques where it is necessary to separate ions with the same valence and sign.

Reverse Osmosis is simple, has an ease of operation and is easy to integrate with other systems such as ultrafiltration to produce a hybrid operation. New materials are being developed that are more pH, temperature, and chlorine resistant than traditional cellulose acetate membranes. Thin-film-composite membranes have led to increase flux performance and enhanced separation. The RO process is affected by the system pressure, feed concentration, pH, presence of other competing ions that may affect extractability.

Ultrafiltration and microfiltration are systems that rely on pore size of the membrane to filter a given feed stream. They are driven by the differential pressure across the system. These systems have been applied to the removal of dilute metals from industrial applications.

An important feature of membrane technologies is the option of hybridization with other systems. This allows for the design of a system that is geared solely toward the removal of the metal of interest in the most effective and efficient method possible.

6.3 Biotechnology

Biological systems are most likely to succeed in areas where established competition does not exist or where a significant advantage can be identified (e.g. low metal concentrations or where different selectivities are required) [3].

Biotechnology offers numerous advantages over traditional treatment processes. With a moderate capital investment this process allows for low operating costs, simple equipment, and maintenance procedures. Additionally, biotechnology may be able to offer high selectivity allowing targeting of specific heavy-metal ions. Depending on the micro organism used, perhaps the greatest advantage biotechnology has over any other technology is the fact that it is completely non-toxic. It can be used to treat waste without the risk of leaving behind a more toxic and difficult problem to deal with.

Although biotechnology offers many advantages, it has not been put into practice as much as other technologies. This means that there is less industry experience dealing with biomaterials. One of the road blocks biotechnology faces is the potential for inconsistency in performance. The many variables that influence the performance of the bioprocess may lead to slow reaction times and less recovery than other processes. Additionally, the availability of the most effective microorganism for a particular application may be problematic.

Some commercial-scale bioprocessing facilities are successful today. Some of these facilities use biotechnology to treat dilute waste streams.

6.4 Qualitative Comparison

The comparison of waste treatment methods is sensitive to various parameters including chemical composition, flux, desired treatment time and allowable cost relative to the specific waste being treated. A detailed scientific comparison of methods based on the specifics of the effluent stream and the environmental circumstances is required for treatment type selection. This section qualitatively evaluates the three types of treatment technologies at a high level, outlining typical comparison parameters. It may be used as a guideline to frame a scientific evaluation of treatment methods.

The evaluation criteria can be broken into 4 categories: technical feasibility; compatibility with existing technology; environmental and safety considerations and cost [89].

Technical feasibility: This category refers to the amount of effort required to install and maintain the technology. If it is technology already in use and has a respectable track record then the effort level to install and maintain it would be minimal. Alternatively, a technology without a history of performance may require piloting operations and tailoring to the specific application. As such the effort level would be higher. Additionally, while in operation if the method is autonomous as opposed to requiring multiple operators, the maintenance effort is less.

Compatibility with existing technology: The impact of the application of a separation technology on a waste stream on the operation of a plant must be positive or minimal.

Environmental and Safety Considerations: At the separation point, any safety concerns (human exposure) due to the technology must be considered. Past the separation point the effluent properties can be compared on levels of toxicity, volume,

greenhouse gas emissions, solid or liquid waste disposal (transportation and/or storage) and total energy consumption.

Cost: The overall capital and operational costs associated with each technology can be compared. It is difficult to obtain comparable cost data for the various technologies available in industry for a given effluent treatment system. Costs are dependent on a number of parameters including:

- concentration of metals in solution
- operational mode of the equipment
- process conditions
- secondary treatments needed (such as regeneration of ion-exchange resins)
- selectivity of ion-exchange resin, membranes, and micro-organisms coupled with their respective capacities for the given metal(s)
- disposal of secondary wastes such as sludges

Figure 6.1 summarizes the high level comparison. Note that the table is not completely populated since some require more specific information about the waste stream.

Eccles [3] outlines performance characteristics of heavy metal removal using separation technologies, some of which were covered in this thesis. Parameters used to compare the technologies include pH, metal selectivity, influence of suspended solids, tolerance of organic molecules and the working level for the appropriate.

Depending upon the objectives of a person selecting a separation technology the outcome of the evaluation may vary. For example, if an owner is not comfortable

Table 6.1: Performance Characteristics of Heavy Metal Removal / Recovery Technologies [3]

Technology	Performance Characteristics				
	pH change	Metal selectivity	Influence of suspended solids	Tolerance of organic molecules	Working level for appropriate metal (mg/l)
Adsorption	Limited	Moderate	Fouled	Can be poisoned	< 10
Electrochemical	Tolerant	Moderate	Can be engineered to tolerate	Can be accommodated	> 10
Ion exchange	Limited	Chelate - resins can be selective	Fouled	Can be poisoned	< 100
Membrane	Limited	Moderate	Fouled	Intolerant	>10
Precipitation					
(a) Hydroxide	Tolerant	Non-selective	Tolerant	Tolerant	> 10
(b) Sulphide	Limited	Limited selective pH dependent	Tolerant	Tolerant	>10
Solvent extraction	Some systems pH tolerant	Metal selective extractants available	Fouled	Intolerant	> 100

Category	Criterion	Process		
		Ion Exchange	Membrane Separation	Biotechnology
Technical Feasibility	Proven Technology	Widely accepted	Gaining momentum	Largely unproven, technology not at a commercial level
	Process Sensitivity	Resin must be matched to application	Membrane/surfactant must be matched to application	Biomaterial must be selected to match application
	Additional Testing Requirements	Resin selection requires testing	Membrane selection requires testing	Identifying the right microorganism is a challenge and requires testing
	Installation	Well understood installation and maintenance procedures	Modular in construction	Dependant upon biomaterial utilized
	Maintenance	Process requires maintenance procedures (rinsing and backwashing)	Maintenance of membrane required	Organic material may need maintenance however it can be relatively autonomous
	Treatment Capacity	Requires Specific Information		
	Treatment Efficiency	With the proper resin this method offers selectivity, efficiency, flexibility	With the proper membrane /surfactant this method offers selectivity, efficiency, flexibility	With the proper biomaterial, this method offers selectivity, efficiency, flexibility
	Flexibility			
Compatability	Impacts on other Operations	Operating temperatures are limited which may interfere with operations	Effective over a larger range of pH values	Operating temperatures are limited
		Turbidity can cause high pressure drops to overcome	No more issues identified	No more issues identified
Environment and Safety	Toxicity of Effluent	Requires Specific Information		
	Volume of Effluent			
	Waste Products	Not identified	20-50 times decrease in waste volumes	Not identified
	Energy	Low energy requirements	Not identified	Low Energy requirements
	Disposal of waste	Requires Specific Information		
	Safety Issues	No safety hazard identified		
Cost	Capital Cost	Stated as a cost effective technology for dilute waste streams	Not identified	Moderate capital cost
	Operational Cost	Not identified	Not identified	Low maintenance cost

Figure 6.1: Qualitative Technology Comparison

with piloting new technology it may be necessary to weight the criteria for 'Proven Technology' highly relative to other criteria which would favor ion exchange. On the other hand, if some evidence supports utilizing biotechnology for the specific waste stream then the risk involved with testing a new technology may balance with the potential reward of a cheap and efficient system to treat the waste stream.

6.5 Conclusions

This is a general overview of potential technologies. Elimination of any technology requires further research and additional information regarding the specifics of INCO's waste stream. Based on research conducted, a qualitative comparison is presented in Figure 6.1. Four categories were used to compare and contrast the three separation technologies that are the primary focus of this research. The figure demonstrates that ion exchange is the most widely accepted and researched technique. It is also flexible in that resin selection can be altered to meet process demands and has well understood installation, maintenance and operational procedures and has low energy requirements. This is the personal view of the author and does not eliminate membrane or biotechnologies from future research. With ion exchange, once the waste stream constituents are identified, one would have to determine a suitable resin through laboratory testing and proceed with column design (number of stages, backwash requirements and regeneration specifics, materials of construction, as well as process conditions such as temperature, pressure, pH, etc.) based on the details of the waste stream.

Chapter 7

Conclusions

Hydrometallurgical processes are in use on a global level to extract metals from ores, concentrate, and other intermediate products. Although hydrometallurgy is a mature technology, numerous advancements in the field have been achieved throughout the past decade.

These advancements eliminate the smelting of ores, lower operating costs, and increase overall quality of metals being produced by eliminating the inefficiencies in the hydrometallurgical process. This leads to the reduction of by-products such as emission of SO_2 gas into the environment, makes hydrometallurgy a more economically viable technology, and lowers the loss of product potentially decreasing the amount of contaminants, toxicity, or both, in the effluent stream.

In a typical hydrometallurgical process, waste streams can potentially be treated for metal recovery. By treating the waste streams using technologies such as ion-exchange, membrane separation, or bio-technology, it is possible to recover valuable metals previously perceived to be uneconomical.

It is difficult to obtain comparable cost data for the various technologies for a given

treatment system. Costs are dependent on a number of parameters including:

- concentration of metal(s) in solution
- operational mode of the equipment (i.e. autonomous or manual)
- process conditions
- required secondary treatment(s) (i.e. regeneration)
- selectivity of ion-exchange resins, membranes, or micro-organisms coupled with their capacity for the metal(s)
- disposal of secondary wastes (i.e. sludge)

7.1 Recommendations

This research provides the fundamental background on a number of treatment technologies available for treating effluent streams from metal processing facilities. Once the specific details of the INCO hydromet effluent stream become available, a series of analyses can be conducted to prove the viability of each technology and then compare the technologies based on the framework provided in this thesis. The current thesis is a qualitative review of treatment technologies. Greater detail and quantitative evaluation is a major recommendation for future work. This thesis may also be utilized as a compilation of information available in the areas of ion exchange, membrane techniques and biotechnology, to avoid duplication of effort in future work.

Bibliography

- [1] Dreisinger, D. (1990). A Challenge for the 1990s: The Hydrometallurgical Treatment of Wastes and Residues. Journal of Metals, 42(1), 27.
- [2] Arbiter, N., & Kellog, H.H. (1985). What the future holds for hydrometallurgy. Eng. Min. J., 152(7), 139-143.
- [3] Eccles, H. (1995). Removal of Heavy Metals from Effluent Streams - Why Select a Biological Process? International Biodeterioration & Biodegradation, 35(1-3), 5-16.
- [4] Lenntech Water Treatment & Air Purification Holding B.V. (n.d.). Lenntech Heavy Metals. Retrieved June 1, 2006, from <http://www.lenntech.com/heavy-metals.htm>
- [5] McGarvey, F.X., & Siber, A. (1985). Removal and Recovery of Metals by Ion Exchange. *Sybron Chemical Inc.*. Retrieved December 2, 2004, from <http://www.ion-exchange.com/service/pdf/reprints/Removal-Recovery-Metals.pdf>
- [6] Government of Newfoundland and Labrador. (2002). Backgrounder: Voisey's Bay Deposit. Retrieved August 1, 2005, from <http://www.releases.gov.nl.ca/releases/2002/crec/0611n02.htm>
- [7] Inco Ltd. (n.d.). Development Projects (Voisey's Bay Nickel Deposit). Retrieved August 1, 2005, from <http://www.inco.com/about/development/voisey/>
- [8] Voisey's Bay Nickel Company Limited (VBNC). (2004). Retrieved August 1, 2005, from <http://www.vbnc.com>
- [9] Inco Ltd. (n.d.). Inco Backgrounder: Hydromet Processing. Retrieved August 1, 2005, from <http://www.inco.com/about/development/voisey/pdf/Hydromet-Backgrounder.pdf>

- [10] Voisey's Bay Nickel Project. (2004). Voisey's Bay Nickel Company Project Description and Project Registration. Retrieved August 14, 2007, from [http : //www.vbnc.com/PDFs/CommercialProcessingPlantRegistration.pdf](http://www.vbnc.com/PDFs/CommercialProcessingPlantRegistration.pdf)
- [11] Voisey's Bay Nickel Company. (2002). Voisey's Bay Nickel Project: Argentia Hydrometallurgical Demonstration Plant Project Registration. Retrieved October 1, 2004, from [http : //www.vbnc.com/Reports/RegistrationDocument.pdf](http://www.vbnc.com/Reports/RegistrationDocument.pdf)
- [12] Rosenqvist, T. (1974). Principles of Extractive Metallurgy. New York: McGraw Hill.
- [13] Phelps Dodge Corporation. (2004). Phelps Dodge Glossary. Retrieved June 1, 2006, from [http : //www.phelpsdodge.com/Glossary/Glossary.htm](http://www.phelpsdodge.com/Glossary/Glossary.htm)
- [14] Mijangos, F., & Diaz, M. (1990). Ion Exchange Recovery of Metals from Waste Water of Complex Sulfide Hydrometallurgy. Hydrometallurgy, 23(2-3), 365-375.
- [15] Environment Canada. (2002). Status Report on Water Pollution Prevention and Control in the Canadian Mining Industry 1999-2000. Retrieved August 1, 2005, from [http : //www.ec.gc.ca/NOPP/docs/rpt/1mm9/1mm9-c.pdf](http://www.ec.gc.ca/NOPP/docs/rpt/1mm9/1mm9-c.pdf)
- [16] Natural Resources Canada. (2003). Mine Environmental Neutral Drainage (MEND). Retrieved August 1, 2005, from [http : //www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/mend/default_e.htm](http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/mend/default_e.htm)
- [17] Natural Resources of Canada. (2003). Mine Waste Management. Retrieved August 1, 2005, from [http : //www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/enviro/waste/waste-c.htm](http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/enviro/waste/waste-c.htm)
- [18] Wase, D.A., & Forster, C. (1997). Biosorption of Metal Ions. London, UK: Taylor & Francis Ltd.
- [19] Health Canada. (2004). Cadmium. Retrieved August 1, 2005, from [http : //www.hc-sc.gc.ca/ewh-scmt/pubs/water-eau/doc_sup-appui/cadmium/index_e.html](http://www.hc-sc.gc.ca/ewh-scmt/pubs/water-eau/doc_sup-appui/cadmium/index_e.html)
- [20] Environment Canada. (2004). Canadian Environmental Quality Guidelines. Retrieved August 1, 2005, from [http : //www.ec.gc.ca/CEQG-RCQE/English/default.cfm](http://www.ec.gc.ca/CEQG-RCQE/English/default.cfm)
- [21] Government of Canada. (1986). Chromium. Retrieved August 1, 2005, from [http : //dsp-psd.pwgsc.gc.ca/Collection/H48-10-1-29-1986E.pdf](http://dsp-psd.pwgsc.gc.ca/Collection/H48-10-1-29-1986E.pdf)

- [22] Mindler, A.B. (1956). Ion Exchange Technology: Chapter 12 - Applications in Hydrometallurgy, in Ion Exchange Technology. New York, N.Y.: Academic Press.
- [23] Kumin, R. (1969, April). Ion Exchange for the Metal Products Finisher - Part I. Product Finishing, 66-73.
- [24] Kumin, R. (1969, May). Ion Exchange for the Metal Products Finisher - Part II. Product Finishing, 71-79.
- [25] Kumin, R. (1969, June). Ion Exchange for the Metal Products Finisher - Part III. Product Finishing, 182-190.
- [26] Mijangos, F., Lombrana, J., Varona, F. & Diaz, M. (1990). Extraction of Non Ferrous Metals from Hydrometallurgical Waste Waters. Planning Product Recycling Using Separation Techniques. Proceedings of the Institution of Chemical Engineers Symposium Series No.119, 61-78.
- [27] The DOW Chemical Company. (1995). DOWEX Resins for Separation of Copper from Liquid Media. Retrieved August 1, 2005, from [http : //www.dow.com/liquidseps/prod/pt_cu.htm](http://www.dow.com/liquidseps/prod/pt_cu.htm)
- [28] The DOW Chemical Company. (1995). DOWEX Ion Exchange Resins. Retrieved August 1, 2005, from [http : //www.dow.com/PublishedLiterature/dh000a/09002f138000a5c9.pdf?filepath = liquidseps/pdfs/noreg/177 - 01721.pdf&fromPage = GetDoc](http://www.dow.com/PublishedLiterature/dh000a/09002f138000a5c9.pdf?filepath=liquidseps/pdfs/noreg/177-01721.pdf&fromPage=GetDoc)
- [29] The DOW Chemical Company. (1995). Tech Facts. Retrieved August 1, 2005, from [http : //www.dow.com/PublishedLiterature/dh01a7/09002f13801a7d98.pdf?filepath = liquidseps/pdfs/noreg/016 - 00003.pdf&fromPage = GetDoc](http://www.dow.com/PublishedLiterature/dh01a7/09002f13801a7d98.pdf?filepath=liquidseps/pdfs/noreg/016-00003.pdf&fromPage=GetDoc)
- [30] Leinonen, II. (1999). Removal of Harmful Metals from Metal Plating Waste Waters Using Selective Ion Exchangers. Retrieved May 27, 2006, from [http : //ethesis.helsinki.fi/julkaisut/mat/kemia/vk/leinonen/removal.pdf](http://ethesis.helsinki.fi/julkaisut/mat/kemia/vk/leinonen/removal.pdf)
- [31] Barros, M.A.S.D., Zola, A.S., Arroyo, P.A., Sousa-Aguiar, E.F., Tavares, C.R.G. (2003). Binary Ion Exchange of Metal Ions in Y and X Zeolites. Brazilian Journal of Chemical Engineering, 20 (04) 413-421.
- [32] REMCO Engineering. (2004). Ion Exchange - Basic Concepts. Retrieved December 14, 2004, from [http : //www.remco.com/ix.htm](http://www.remco.com/ix.htm)
- [33] DMP Corporation. (n.d.). Ion Exchange Removes Metals from Wastewater. Retrieved December 1, 2004, from [http : //www.dmpcorp.com/pdf/Ion_Exchg_PDX.pdf](http://www.dmpcorp.com/pdf/Ion_Exchg_PDX.pdf)

- [34] Brown, C.J. (2002). Micro-Media Filtration: An Alternative to Membrane Filtration. Retrieved June 1, 2005, from [http : //www.cco - tec.com/tcchpapers/TP%20160%20Micro%20Filtration.pdf](http://www.cco-tec.com/tcchpapers/TP%20160%20Micro%20Filtration.pdf)
- [35] Wheaton, R.M., & Lefevre, L.J. (2000). DOWEX Ion Exchange Resins: Fundamentals of Ion Exchange. Retrieved June 1, 2005, from [http : //www.dow.com/PublishedLiterature/dh_0042/09002f138004267a.pdf](http://www.dow.com/PublishedLiterature/dh_0042/09002f138004267a.pdf)
- [36] Seader, J.D., & Henley, E.J. (1998). Separation Process Principles. Hoboken, NJ: John Wiley and Sons Inc.
- [37] Diaz, M., Rendueles, M., Fernández, A. & Suárez. (1998). Hydrometallurgy Wastewater Split-Up by Fluidized-Bed Ion-Exchange Continuous Equipment. Separation Science and Technology, 33(7), 1025-1042.
- [38] Wierchowski, S. (1995). Ion Exchange Resins Retrieved June 1, 2006, from [http : //www.rpi.edu/dept/chem - eng/Biotech - Environ/IONEX/resins.htm](http://www.rpi.edu/dept/chem-eng/Biotech-Environ/IONEX/resins.htm)
- [39] De Villiers, P., Van Deventer, V. & Lorenzen, L. (1997). The Use of Ion-Exchange Resins for the Recovery of Valuable Species from Slurries or Sparingly Soluble Solids. Minerals Engineering, 10(9), 929-945.
- [40] Price, G. (n.d.). TU Chemical Engineering Zeolite Page. Retrieved June 1, 2006, from [http : //www.personal.utulsa.edu/geoffrey - price/zeolite/zeo_narr.htm](http://www.personal.utulsa.edu/geoffrey-price/zeolite/zeo_narr.htm)
- [41] Minerals Gallery. (1995). The Zeolite Group of Minerals. Retrieved April 28, 2005, from [http : //mineral.galleries.com/minerals/silicate/zeolites.htm](http://mineral.galleries.com/minerals/silicate/zeolites.htm)
- [42] Blanchard, G., Maunaye, M., and Martin, G. (1984). Removal of Heavy Metals from Water by Means of Natural Zeolites. Water Research, 18(2), 1501-1507.
- [43] Faghihian, H., Ghannadi Maragheh, M., & Kazemian, H. (1999). The Use Of Clinoptilolite and its Sodium form for Removal of Radioactive Cesium, and Strontium from Nuclear Waterwater. Applied Radiation and Isotopes, 50(2), 655-660.
- [44] North America's Zeolite. (n.d.). Wastewater Treatment. Retrieved June 1, 2006, from [http : //www.zeolite.ca/WasteWaterTreatment.htm](http://www.zeolite.ca/WasteWaterTreatment.htm)
- [45] Ouki, S.K. & Kavannagh, M. (1997). Performance of Natural Zeolite for the Treatment of Mixed Metal Contaminated Effluents. Waste Management & Research, 15, 383-394.

- [46] Meyers, P. (1999). Applications of Weak Acid Cation Resin in Waste Treatment. Retrieved June 1, 2006, from <http://www.resintech.com/Content/TechArticles/Applications%20of%20Weak%20Acid%20Cation%20Resin%20in%20Waste%20Treatment.pdf>
- [47] Ion Exchange Media: Serdolit Chelating Resins. (n.d.). Retrieved June 1, 2006, from <http://www.tecimport.com.br/Serva2004/products/knowledge/071117.html>
- [48] Chakhashiri, B. (n.d.). Chemicals of the Week: Chelates and Chelating Agents. Retrieved June 1, 2006, from <http://scifun.chem.wisc.edu/chemweek/Chelates/Chelates.html>
- [49] Ewing, W., Evans J.W., & Doyle, F.M. (2003). The Effect of Plating Additives on the Recovery of Copper from Dilute Aqueous Solutions Using Chelating Resins: Proceedings of the 5th International Symposium on Hydrometallurgy., Vancouver, B.C. 753-762.
- [50] Suzuki, M. (2004). Activated Carbon Adsorption for Treatment of Agrochemicals in Water. Retrieved June 1, 2006, from <http://landbase.hq.unu.edu/Symposia/2001Symposium/abstracts/06Suzuki.htm>
- [51] Perry, R.H., Greenm D.W., & Maloney, J.O. (1999). Perry's Chemical Engineers' Handbook. New York: McGraw-Hill.
- [52] Ho, W.S. & Sirkar, K.K. (1992). Membrane Handbook. New York: Van Nostrand Reinhold.
- [53] Strathmann, H. (2001, May). Membrane Separation Processes: Current Relevance and Future Opportunities. AIChE Journal, 47(5), 1077-1087.
- [54] Srikanth, G., Technology Information, Forecasting & Assessment Council (TIFAC). (n.d.). Membrane Separation Processes. Retrieved June 9, 2005, from <http://www.tifac.org.in/news/mcmb.htm>
- [55] Geankopolis, J.C. (2003). Transport Processes and Separation Process Principles: Includes Unit Operations, Fourth Edition. Upper Saddle River, NJ: Prentice Hall.
- [56] Yang, X.J., Fane, A.G., & Soldenhoff, K. (2003). Comparison of Liquid Membrane Processes for Metal Separations: Permeability, Stability, and Selectivity. Ind. Eng. Chem. Res. 42, 393-403.
- [57] Application of Liquid Emulsion Membrane for Wastewater Treatment in Chemical Industry. Retrieved June 9, 2005, from <http://www.ficci.com/cicnew/techoption/Application.htm>

- [58] Abou-Nemeh, I. & Van Peteghem, A.p. (1992). Extraction of Multi-Component Systems of Metals from Simulated and Industrial Effluents by Liquid Surfactant Membranes (LSM). Hydrometallurgy, 31, 149-162.
- [59] Xu, T. (2001). Development of Bipolar Membrane-Based Process. Desalination, 140, 247-258.
- [60] Tsuru, T., Nakao, S. & Kimura, S. (1995). Ion Separation by Bipolar Membranes in Reverse Osmosis. Journal of Membrane Science, 108, 269-278.
- [61] Marchese, J., Campderrós, M. & Acosta, A. (1995). Transport and Separation of Cobalt, Nickel and Copper Ions with Alanine Liquid Membranes. Journal of Chemical Technology and Biotechnology, 64, 293-297.
- [62] Draxler, J., Fürst, W. & Marr, R. (1988, September). Separation of Metal Species by Emulsion Liquid Membranes. Journal of Membrane Science, 38(3), 281-293.
- [63] Boyadzhiev, L. & Kyuchoukov, G. (1980). Further Development of Carrier-Mediated Extraction. Journal of Membrane Science, 6, 107-112.
- [64] Dalea, V., Masu, S., Bogatu, C., & Manea, F. (n.d.). Membrane Separation Processes for Wastewater Treatment. Retrieved August 1, 2005, from [http : //www.ichmt.org/abstracts/MFTP – 2000/abstracts/49.pdf](http://www.ichmt.org/abstracts/MFTP-2000/abstracts/49.pdf)
- [65] Ozaki, H., Sharma, K., Saktaywin, W. (2002). Performance of an Ultra-Low-Pressure Reverse Osmosis Membrane (ULPROM) for Separating Heavy Metal: Effect of Interference Parameters. Desalination, 144, 287-294.
- [66] Tavares, C.R., Vieira, M., Petrus, J.C.C., Bortoletti, E.C., & Ceravollo, F. (2002). Ultrafiltration/ Complexation Process for Metal Removal from Pulp and Paper Industry Wastewater. Desalination, 144, 261-265.
- [67] Atamaneko, I.D., Kryvoruchko, A.P., Yurlova, L.Y., & Kornilovich, B.Y. (2003). Concentration of Heavy Metal by Pressure Driven Membrane Methods. Desalination, 158, 151-156.
- [68] Benito, Y., & Ruiz, M.L. (2002). Reverse Osmosis applied to metal finishing wastewater. Desalination, 142, 229-234.
- [69] Kitagawa, T., Nishikawa, Y., Frankenfeld, J. & Li, N. (1977). Wastewater treatment by liquid membrane process. Environmental Science & Technology, 11(6), 602-605.
- [70] McNew, E.B., Barnes, J.M. & Torma, A.E. (1992). A Biosorption Approach to Removal of Trace Concentrations of Uranium and Heavy Metals from Aqueous Solutions: Proceedings of the Symposium on Emerging process Technologies for a Cleaner Environment. Phoenix, Arizona.

- [71] ANSTO. (2001). Biooxidation Heap Leaching. Retrieved August 1, 2005, from [http : //www.ansto.gov.au/sulfide/biooxidation.html](http://www.ansto.gov.au/sulfide/biooxidation.html)
- [72] Cribb, J. (2002). Biomining: The Next Mineral Revolution. CSIRO (Commonwealth Scientific and Industrial Research Organisation) Retrieved August 1, 2005, from [http : //www.csiro.au/index.asp?type=featureArticle&id=BioMining](http://www.csiro.au/index.asp?type=featureArticle&id=BioMining)
- [73] Johnson, D.B. (2001). Importance of Microbiology in the Development of Sustainable Technologies for Mineral Processing and Wastewater Treatment. Hydrometallurgy, 59(2-3), 147-157.
- [74] Ahalya, N., Ramachandra, T.V., & Kanamadi, R.D. (n.d.). Biosorption of Heavy Metals. Retrieved August 1, 2005, from [http : //144.16.93.203/energy/water/paper/biosorption/biosorption.htm](http://144.16.93.203/energy/water/paper/biosorption/biosorption.htm)
- [75] Harvey, T. (2005). It's a bug's life. Retrieved August 1, 2005, from [http : //technology.informinc.com/biomctmine/biopapers/biomct_issues.pdf](http://technology.informinc.com/biomctmine/biopapers/biomct_issues.pdf)
- [76] Ruiz-Manríquez, A., Magaña, P.I., López, V., & Guzmán, R. (1997). Biosorption of Cu by *Thiobacillus ferrooxidans*. Bioprocess Engineering, 18, 113-118.
- [77] Baig, T.H., Garcia, A.E., Tiemann, K.J., & Gardea-Torresdey, J.L. (1999). Adsorption of Heavy Metal Ions by the Biomass of *Solanum Elaeagnifolium* (Silverleaf Night-Shade): Proceedings of the 1999 Conference on Hazardous Waste Research. Retrieved August 1, 2005, from [http : //www.cngg.ksu.edu/HSRC/99Proceed/gardeatorresdey2.pdf](http://www.cngg.ksu.edu/HSRC/99Proceed/gardeatorresdey2.pdf)
- [78] Mihova, St., Godjevargova, T. (2001). Biosorption of Heavy Metals from Aqueous Solutions. Retrieved August 1, 2005, from [http : //www.ejournalnet.com/Contents/Issuc_1/6/62001.htm](http://www.ejournalnet.com/Contents/Issuc_1/6/62001.htm)
- [79] Smith, R.W., & Misra, M. (1993). Bioprocessing of minerals: Proceedings of the 1993 Paul E. Queneau International Symposium, Denver, Colorado, 1015-1037.
- [80] Brandl, H. (n.d.). 8 Microbial Leaching of Metals. Retrieved August 1, 2005, from [http : //www.wiley-vch.de/books/biotech/pdf/v10-bran.pdf](http://www.wiley-vch.de/books/biotech/pdf/v10-bran.pdf)
- [81] Walting, H. (2003, September). Mineral Bio-Processing of Copper Sulfides. AusIMM Bulletin, 5, 28-33.
- [82] Keskinan, O., Goksu, M.Z.L.; Basibuyuk, M. & Forster, C.F. (2004, April). Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*). Bioresource Technology, 92(2), 197-200.

- [83] Brierley, J.A. & Brierley, C.L. (1993). Reflections on and Considerations for Biotechnology in the Metals Extraction Industry. Hydrometallurgy: Fundamentals, Technology, and Innovations, Society of Mining, Metallurgy, and Exploration, 647-660.
- [84] Clark, T. & Ehrlich, H. (1992). Copper Removal from an Industrial Waste by Bioleaching. Journal of Industrical Microbiology, 9(3-4), 213-218.
- [85] Ehrlich, H.L. (1991, June). Microbes for Biohydrometallurgy: Proceedings of the Conference Mineral Bioprocessing, 27-41.
- [86] Torma, A.E. (1991, June). New Trends in Biohydrometallurgy: Proceedings of the Conference Mineral Bioprocessing, 43-55.
- [87] Boonstra, J. & Buisman, C.J.N. (2003). Biotechnology for Sustainable Hydrometallurgy: Hydrometallurgy 2003 - Proceedings of the Conference Mineral Bioprocessing, 2, 1105-1119.
- [88] White, C. & Wilkinson, S. & Gadd, G. (1995). The Role of Microorganisms in Biosorption of Toxic Metals and Radionuclides. International Biodeterioration & Biodegradation, 17(40), 17-40.
- [89] Thanyamanta, W. & Hawboldt, K. & Husain, T., et al. Evaluation of Offshore Drilling Cuttings Management Technologies Using Multicriteria Decision Making. Environmental Management, 141.



